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Author: Kine Ims	Signature of Author: 
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Abstract

Constructed wetlands are created for the purpose of treating anthropogenic discharges, such as agricultural and urban runoff to reduce the potential of undesirable effects in receiving waters. Leikvollbekken is a mature constructed wetland located in north-west of Store Stokkavatnet in Stavanger Municipality. The wetland is a two-pond free water surface system constructed with the aim to reduce excessive nitrogen and phosphorus in the pelvis before reaching Store Stokkavatnet. The main focus of this thesis was to monitor the constructed wetland with respect to nitrogen. Nitrogen removal in the wetland was believed to occur through biological assimilation and dissimilation. The hypothesis was that the degree of retention would depend on flow, resulting in a positive retention over time.

With some exceptions, weekly water samples were collected in the period October 2018 to May 2019 in inlet, mid-pond and outlet of the wetland. Flow in and out of the wetland was measured with an interval of 15 minutes during the thesis period by an integrated flow meter at site. Grab samples from Store Stokkavatn and Madlabekken were included in a period to compare concentrations with water in Leikvollbekken. In addition, a storm event was included to investigate the effect of high hydraulic loadings on incoming concentrations. Water samples were analyzed for total nitrogen, nitrate and ammonium. Total and fixed suspended solids, pH, conductivity, alkalinity and color were included to investigate if any significant correlations existed with nitrogen concentrations in the samples taken.

The overall results showed higher concentrations in Leikvollbekken compared to Store Stokkavatn and Madlabekken. A positive retention of 9.4 % TN (68.6 kg), 6.1 % NO_3^- (33.8 kg) and 87.1% NH_4^+ (7.2 kg) was observed during the period studied. Highest concentrations were observed during the storm event. An interesting observation was the increasing concentrations of TN, NO_3^- and NH_4^+ in mid-pond and outlet samples in April and during the storm event, indicating contribution from additional sources than the inlet water. No significant correlation between average flow per sampling and total nitrogen was found. Moreover, no connection was found between nitrogen compounds and the additional parameters except conductivity and color.

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Abbreviation list

BWE	Backward elimination
BMP	Best Management Practice
FSS	Fixed suspended solids
FWS	Free Water Surface
HSSF	Horizontal Sub-Surface Flow
VF	Vertical Flow
HRT	Hydraulic Retention Time
ISA	Ionic Strength Adjustor
ISE	Ion-Selective Electrode
sTN	Soluble total nitrogen
TN	Total nitrogen
TSS	Total suspended solids

1. Introduction

Agricultural and urban runoff contains nutrients, pesticides, microbes and sediments causing undesirable water quality in receiving waters (A.-G. B. Blankenberg, Haarstad, & Paruch, 2015). Rivers and streams are in particular susceptible as they are easily exposed to pollution (Ødegaard & Norheim, 2014). The additional supply of essential plant nutrients such as nitrogen and phosphorus promote eutrophication of surface water and lakes. These are inputs that come in addition to the natural circulation such as weathering of bedrock or leaching of soil (Artsdatabanken, 2019). Agricultural and urban runoff is considered as one of the largest anthropogenic sources of nitrogen, phosphorus and sediment inputs to Norwegian waters (Borgvang, Selvik, Tjomsland, & Eggestad, 2003; Selvik, Tjomsland, Borgvang, & Eggestad, 2006; Solheim et al., 2001). Due to their role in eutrophication, being toxic to aquatic species in too high concentrations and their effect on oxygen content in lakes, are nitrogen compounds considered to be one of the principal constituents of concern in wastewater.

The need to protect ecosystems from eutrophication has led to the implementation of various measures to reduce nutrient loadings in wastewater before entering open water. One of the measures used for this purpose is the construction of artificial wetlands. Wetlands are valuable to society functioning as downstream receivers of wastewater from both human and natural sources. The complex systems are proven to remove nutrients, pollutants and sediments from water by acting as effective “sinks” (Mitsch, 2015). In the past two decades, more than 900 constructed wetlands have been constructed in Norway (A.-G. B. Blankenberg et al., 2015). Given that the artificial wetlands are adequately placed in the landscape, they are considered an extensive, cost-effective and efficient treatment technology for wastewater loadings (Maltais-Landry, Maranger, Brisson, & Chazarenc, 2009).

Monitoring of nutrients in rivers and lakes is necessary for understanding the causes and development of water quality. Quantitatively, nitrogen is an essential nutrient for plant growth, but also a nutrient promoting algal blooms and a common pollutant (A.-G. B. Blankenberg et al., 2015). In previous studies did the wetlands ability to retain nitrogen vary, from showing a low retention efficiency (2%) to being highly efficient (up to 95%) depending on design, inflow loading and climate (Huang, Reneau Jr, & Hagedorn, 2000; Lee, Fletcher, & Sun, 2009; Lin, Jing, Lee, & Wang, 2002; Maltais-Landry et al., 2009; Vymazal, 2007). The extent of nitrogen processes and retention in constructed wetlands are unclear and have significant variations.

More research in this field is needed to increase the performance of nitrogen retention in constructed wetlands and nutrient removal by wetlands in general.

The objective of this thesis was to investigate the nitrogen retention performed by a mature constructed wetland. A storm event was included to investigate how increased hydraulic load would affect the parameters. Nitrate was measured by two different methods during the thesis. Spectroquant Cell Test was used on weekly water samples and ISE Nitrate Electrode was used on samples collected during storm event. Major differences between measured concentrations by the two methods were discovered. Hence, a method evaluation were included in the thesis.

2. Background

This section consists of an introduction to nitrogen's role in eutrophication and why it is of concern, in addition to an introduction of the concept constructed wetlands. Furthermore, nitrogen storage and retention and removal processes are presented. The theory section ends with a subsection presenting the objective of thesis.

2.1 Environmental consequences of excess nutrient supply in aquatic ecosystems

Human activities have resulted in increased fluxes of growth-limiting nutrients from landscape to receiving waters, and are today influencing the world's major aquatic ecosystems to a great extent (Smith, 2003). Eutrophication is considered one of severe kinds of water pollution (Ansari, Singh Gill, Lanza, & Rast, 2011). Initially, it is a natural process occurring in all aquatic systems over thousands of years. However, anthropogenic activities have led to a high rate of nutrients input to the systems, developing the eutrophication condition in a shorter time.

The excessive nutrient input leads to increased productivity in the different levels in food chains (Læg Reid, 1999), resulting in undesirable overgrowth of phytoplankton. Higher primary production forms a layer over the water surface, reducing light penetration and re-oxygenation of water leading to significant changes in the water quality (Ansari et al., 2011). In 2009, only 43% of the surface water in Europe was considered having a good ecological condition (Miljødirektoratet, 2015). Consequences of eutrophication include algal blooms, altered species and diversity, reduced oxygen levels (Miljødirektoratet, 2017), in addition to nitrate emissions to groundwater threatening freshwater quality and ecosystem (Table 1). However, in contrast to the low percentage of good quality surface water in 2009 did the levels of the nutrient in freshwater bodies sink. From 1992 to 2011 did the average levels of phosphorus and nitrogen in Europe decrease by 57% and 20%, respectively, due to improvements in wastewater treatment and regulations (Miljødirektoratet, 2015).

The two most essential nutrients for freshwater eutrophication are phosphorus (mainly) and nitrogen (Miljødirektoratet, 2017; Smith, Joye, & Howarth, 2006). Although nitrogen is a growth-limiting element primarily in marine environments and flooded soils (Mitsch & Gosselink, 2015) are too high nitrogen concentrations undesirable for potential drinking water and a factor for undesirable algae bloom also in freshwater (Miljødirektoratet, 2015). Moreover,

increased nitrogen input are associated with acidification in aquatic systems (Grennfelt & Thörnelöf, 1992).

The environmental condition in rivers and lakes are classified into chemical states based on a number of physical and chemical parameters.

Table 2 shows the chemical state for different total nitrogen concentrations in a clear lake with moderate concentration of calcium carbonate.

Table 1 Presentation of adverse effects due to eutrophication. Modified from (Smith, 2003)

Adverse effects of freshwater and coastal marine eutrophication

- Increased productivity and biomass of phytoplankton and suspended algae
 - Shifts in phytoplankton composition to bloom-forming species, many of which may be toxic, or which may not be consumed effectively by aquatic grazers
 - Increased productivity, biomass, and species composition of attached microalgae (periphyton)
 - Changes in productivity, biomass, and species composition of marine macroalgae
 - Changes in productivity, biomass, and species composition of aquatic vascular plants
 - Reduced yields of desirable finfish and shellfish species
 - Reductions in the health and size for marine coral populations
 - Threats to endangered aquatic species
 - Decreases in water column transparency
 - Taste, odor, and filtration problems in drinking water supplies
 - Depletion of deep-water oxygen
 - Decreases in the perceived aesthetic value of water body
 - Negative economic impacts, including decreased property values and reduced recreational uses
-

Table 2 Defined classes for water quality in a clear lake with moderate concentration of calcium carbonate (Iversen & Sandøy, 2018).

Chemical state	Total nitrogen [$\mu\text{g/L}$]
Great	1-425
Good	425-675
Moderate	675-950
Bad	950-1425
Poor	> 1425

2.2 Anthropogenic sources

Nitrogen compounds are released to air and water from urban areas, agriculture and industry (Figure 2-1). Intensification of agricultural systems have resulted in increased nitrogen input through the use of fertilizers (Miljødirektoratet, 2015). In the case of excess nitrogen supply may nitrogen saturation occur, that is, a smaller fraction of nitrate and ammonium will be able to be absorbed by vegetation and soil in the catchments (Hessen, 2009). Agricultural fields receive water either by natural precipitation or snowmelt, or irrigation. In periods with high hydraulic input, do the land receive water at a higher rate than the infiltration rate by the soil causing the water to enter adjacent water bodies (Lægneid, 1999). The loss of nitrogen from agricultural watersheds have showed to increases significantly with the amount applied (Simmelsgaard, 1998), in addition to vary greatly in between different catchments (Vagstad et al., 2004).

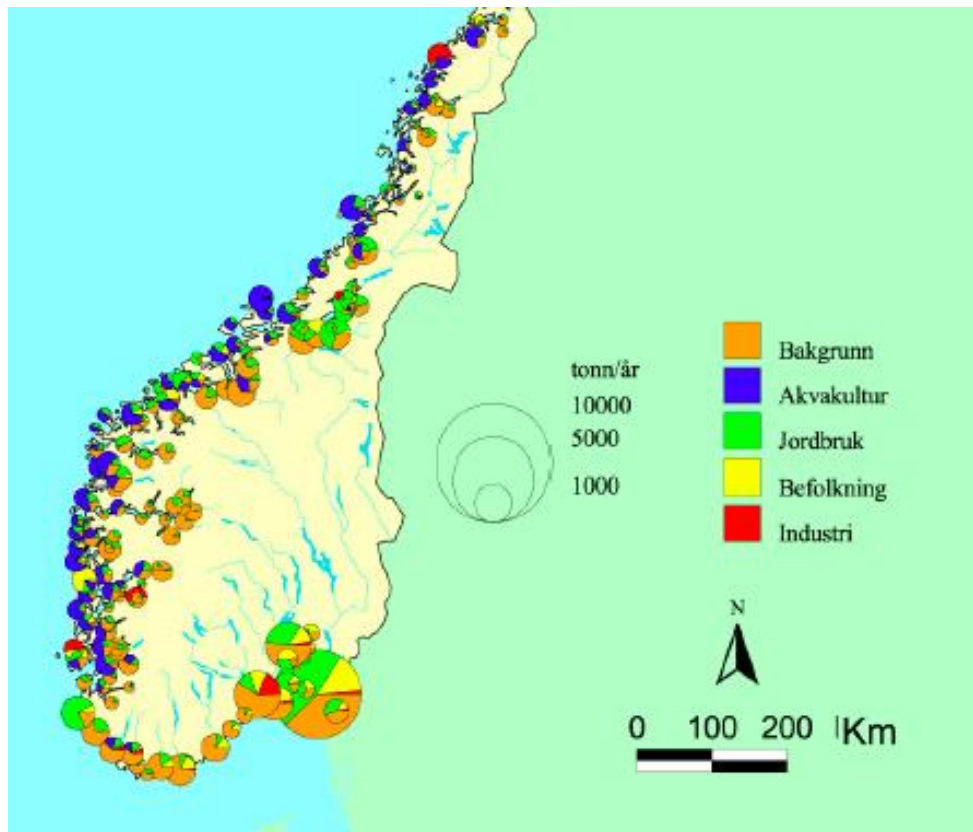


Figure 2-1 The relative size of anthropogenic nitrogen sources to lakes in Norway, 2002 (Borgvang et al., 2003)

2.3 Nitrogen in the environment

The nitrogen cycle illustrates the circulation of various forms through nature (Figure 2-2). Nitrogen is commonly found in the atmosphere as nitrogen gas, in groundwater and soil as nitrate and in biota as amino acids (Økland, 1998). Despite covering 78% of the volume of gases present in the atmosphere, dinitrogen has low chemical activity and therefore of low availability for organisms. The nitrogen from the atmosphere is made possible for uptake by organisms by biological conversion to more chemically active forms through nitrogen fixation by symbiotic and free-living species. Aerobic and anaerobic micro-organisms convert dinitrogen to ammonia using the enzyme nitrogenase. A set of other biochemical processes convert nitrogen into other forms after nitrogen fixation (Howard, 1998).

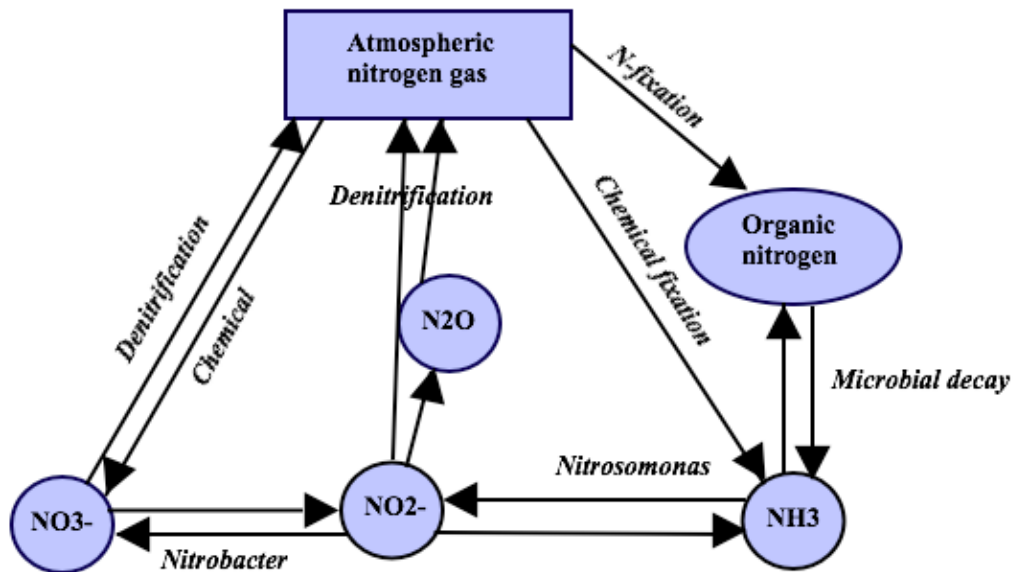


Figure 2-2 The Nitrogen Cycle. Modified from (Howard, 1998).

The atmospheric deposition of nitrogen has major importance for elemental relationships in water (Hessen, 2010). Water is normally saturated with gaseous nitrogen. The solubility of N₂ at 20°C and 1 bar is approximately 20 mg/L, varying between the different compounds (Lenntech B.V., 1998-2019). The form of nitrogen compounds found in the water depends on the water properties in the area.

2.4 Natural wetlands

Wetlands are difficult to define, classify and categorize as they represent transition zones between terrestrial ecosystems and aquatic habitats such as seas and lakes (Cole & Weihe, 2015). The Ramsar convention, also called “Convention on Wetlands (Ramsar, Iran, 1971),” compiled a broad definition of a wetland. The intergovernmental treaty defined a wetland as:

“areas of marsh, fen, peatland or water, whether natural or artificial, permanent or temporary, with water that is static or flowing, fresh, brackish or salt, including areas of marine water the depth of which at low tides does not exceed six meters” (Ramsar Secretariat, 2016).

Wetlands are land areas that during part or all year are wet due to their location in the landscape (Robert H. Kadlec, Wallace, & Knight, 2008). The systems are often located between permanently flooded deep-water aquatic systems such as lakes, rivers, estuaries or oceans, or

as isolated basins with no deep-water systems and little outflow (Mitsch & Gosselink, 2015). The environments with associated plant and animal life are in these areas controlled by water as the primary factor. Wetlands occur in areas where the water table is at or close to the surface of the land, or in areas where land is covered by shallow water (Grobicki, et al., 2016).

The Ramsar Convention presents five major types of wetlands that are generally recognized (Ramsar Secretariat, 2016):

- Marine wetlands (including coastal lagoons, seagrass beds, rocky shores and coral reefs)
- Estuarine wetlands (including tidal marshes and mudflats, deltas and mangrove swamps)
- Lacustrine wetlands (wetlands associated with lakes)
- Riverine wetlands (wetlands located along rivers and lakes)
- Palustrine (wetlands as marshes, swamps and bogs)

Natural wetlands have been receiving wastewater since ancient times. In the 20th century, man-made wetlands were developed to improve the treatment capacity with systems designed to have the desired properties similar to a natural wetland's characteristics (Grobicki, et al., 2016).

2.4.1 Mass balance

The mass balance in a wetland includes all inputs, outputs and cycling within (Figure 2-3). The input of materials occurs through hydrologic, biologic and geologic pathways (Mitsch & Gosselink, 2015). Biologic inputs include nitrogen fixation, photosynthetic uptake of carbon and biotic transport, and geological inputs are due to weathering of parent rock. Hydrologic inputs generally dominate the elemental inputs (Mitsch & Gosselink, 2015).

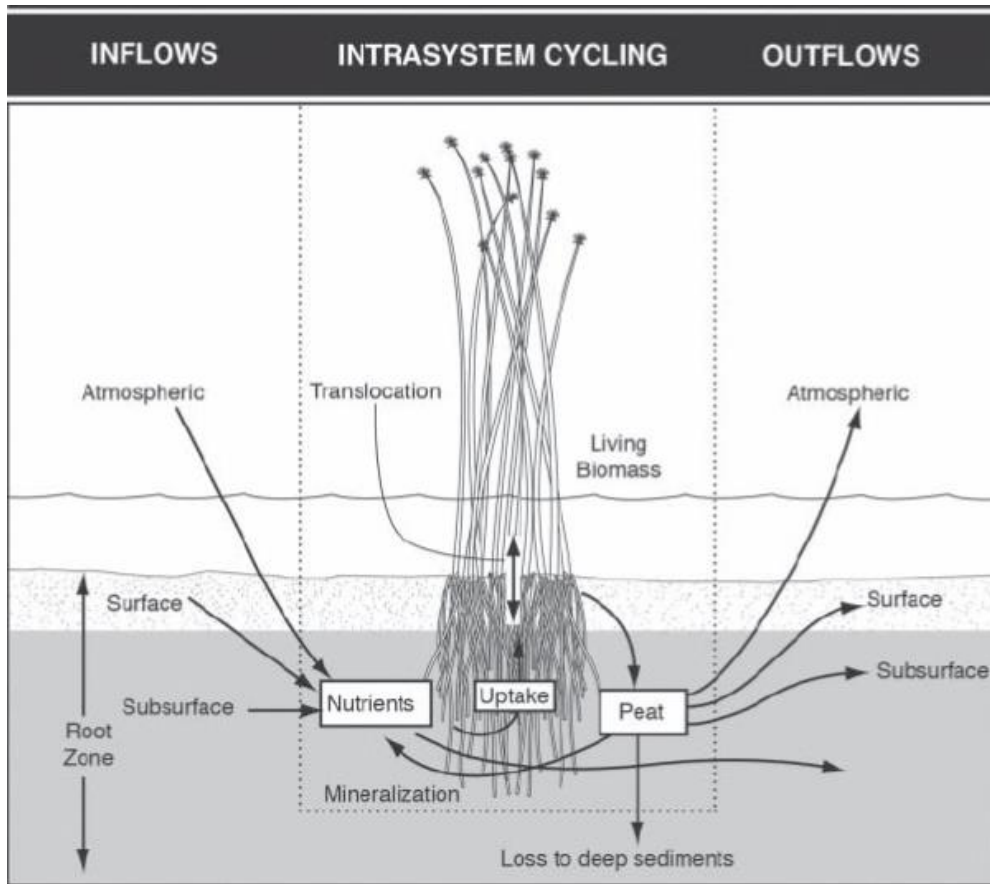


Figure 2-3 The components of a nutrient budget in wetland (Mitsch, 2015)

The hydrology is the most critical determinant of the function of the wetland and affects all ecological processes, including soil chemistry, plant diversity and animal behavior (Cole & Weihe, 2015). Water entering the wetlands comes from seepages in the ground, nearby lakes and streams as runoff or by precipitation (Figure 2-4) (Robert H. Kadlec et al., 2008).

All wetlands have a unique arrangement of hydrology over time. Changing climate patterns and changing volume of water in the system affect the system (Cole & Weihe, 2015) and determine the composition of plant species present (Mitsch & Gosselink, 2015). The hydraulic retention time in the wetland is critical for what interactions and treatment processes that can occur (Robert H. Kadlec et al., 2008).

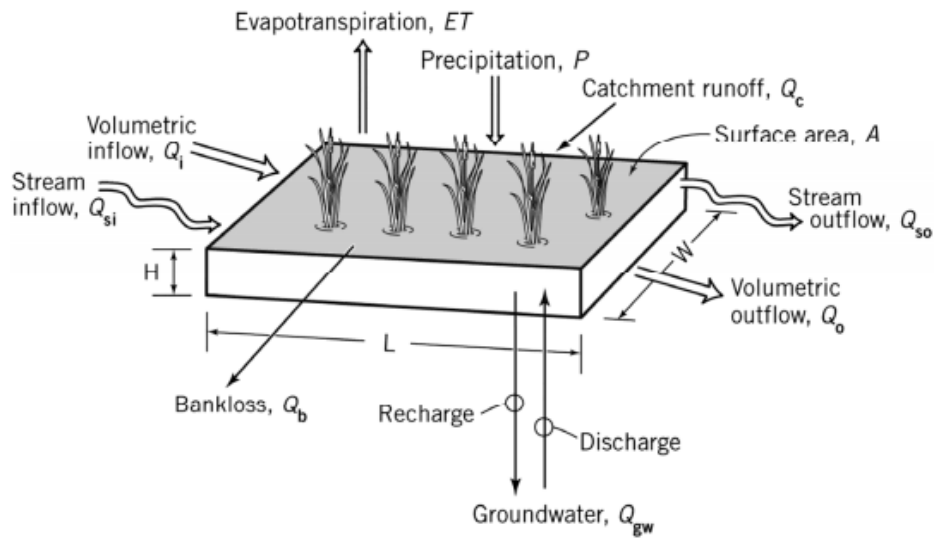


Figure 2-4 The hydrologic budget in a wetland (Robert H. Kadlec et al., 2008)

Artificial wetlands should be designed with the ability to temporarily store higher precipitation events than what is expected (Langergraber et al., 2017).

2.4.2 The nitrogen cycle in wetlands

The nitrogen cycle is considered one of the most studied and important chemical cycles in wetlands (Figure 2-5) (Mitsch & Gosselink, 2015). Nitrogen appears in different oxidation states, involving several microbiological processes in the transformation processes. Major pathways include (Mitsch & Gosselink, 2015):

- Ammonification (mineralization)
- Nitrification
- Denitrification
- Plant uptake
- Anammox (anaerobic ammonium oxidation)
- Ammonia volatilization
- Nitrogen fixation

A selection of the pathways is further described in “3.2 Main removal and retention mechanisms of nitrogen in constructed wetlands.”

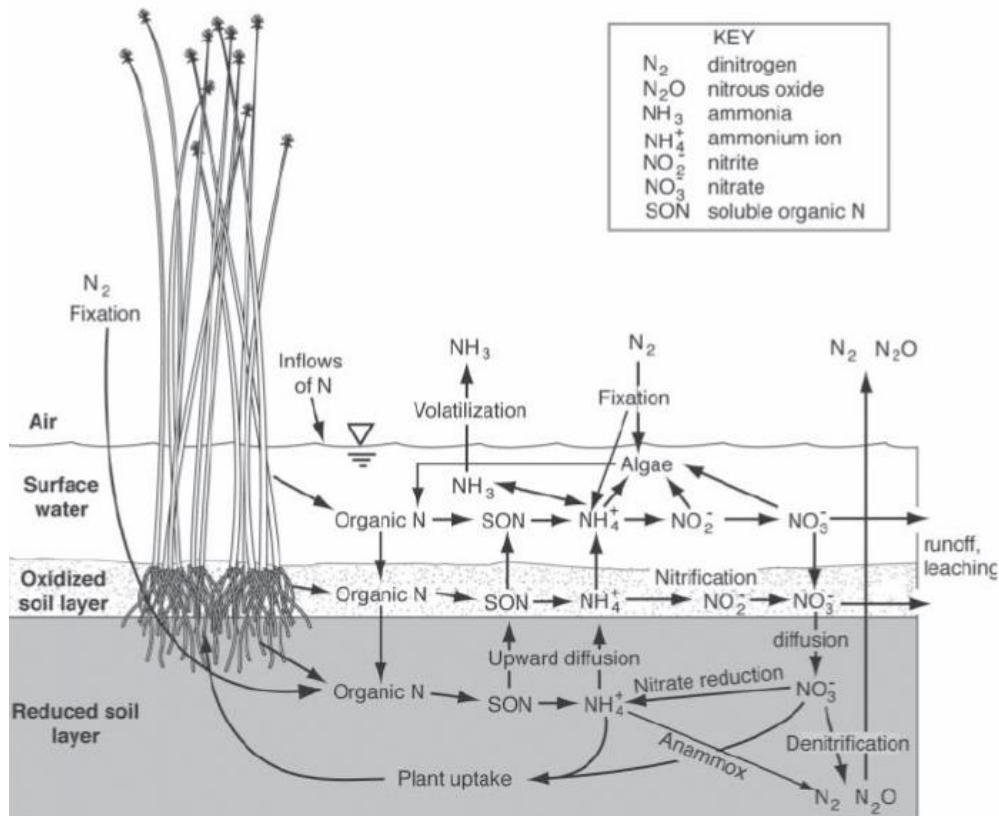


Figure 2-5 The nitrogen cycle in wetlands. (Mitsch & Gosselink, 2015)

2.5 Constructed wetlands

A constructed wetland is defined as:

“Constructed wetlands are multifunctional shallow water detention, pollutant retention structures, constructed with predominately natural materials such as soil, water and biota to facilitate the desirable hydrological, physical, chemical and biological processes of natural wetlands in a controlled manner” (Kandasamy & Vigneswaran, 2008).

Constructed wetlands are artificial systems constructed to treat industrial, municipal and agricultural runoff. The treatment systems are established close to the source to reduce loads of agricultural nutrients, pesticides, microbes and sediments downstream.

2.5.1 Different designs of constructed wetlands

Constructed wetlands are designed depending on the target contaminants. From agricultural fields the principal contaminants considered a threat to receiving ecosystems include nitrate, phosphorus, agricultural chemicals and suspended solids. Concentrations depend on

agricultural fertilization practices, topography and soil type in the area, as well as rainfall intensity. In Norway, studies have shown that vegetated buffer zones and constructed wetlands designed for Nordic climate are good supplements to best management practice (BMP) for retaining and removing nutrients, pesticides and sediments even though they are relatively small treatment systems (A.-G. B. Blankenberg et al., 2015).

Constructed wetlands are classified as either permanent or ephemeral, permanently inundated or periodically drying out, respectively (Kandasamy & Vigneswaran, 2008). The three most common types of are Free water surface (FWS) wetlands, Horizontal subsurface flow (HSSF) wetlands and Vertical flow (VF) wetlands (Robert H. Kadlec et al., 2008). The different types are divided into a large variety of design, such as flow patterns, layout, media and plants. The constructed wetlands in Norway are mainly designed for phosphorus removal due to mainly being the nutrient causing problems for Norwegian freshwater quality by the growth of toxic algae (A.-G. B. Blankenberg et al., 2015). Constructed wetlands in Norway are usually too small to achieve high nitrogen retention (A.-G. Blankenberg, Haarstad, & Søvik, 2008).

Usually, constructed wetlands in Norway are designed with a deeper sedimentation pond at the inlet followed by one or several shallower zones with vegetation. The sedimentation pond function to lower the water velocity and thereby allow incoming particles to settle. The following shallower vegetated area filters the particles escaping from sedimentation pond. The roots stabilize the trapped sediments and prevent resuspension. In addition, plants take up nutrients and utilize them for growing (A.-G. B. Blankenberg et al., 2015).

FWS (Figure 2-6) are wetlands with open water areas, floating vegetation and emergent plants (Robert H. Kadlec et al., 2008). Studies have shown that removal of finer particles in vegetated ponds is more efficient than in non-vegetated ponds (Braskerud et al., 2005). This configuration of a constructed wetland is similar to natural marshes and are suitable in all climates, also in the north. Although, some removal processes are less efficient due to colder temperature in water, which is typical for nitrogen. Partly or total ice formation in water areas may hydraulically hinder the processes at winter time. In contrast, processes such as TSS removal are more efficient under ice than in more temperate seasons (Robert H. Kadlec et al., 2008).

Adsorption, precipitation, sedimentation, filtration, oxidation and reduction processes effect the water flowing through the wetland. Due to the ability to handle pulse flow and changing water levels, this configuration of wetlands is typical in urban, agricultural and industrial stormwater treatment (Robert H. Kadlec et al., 2008).

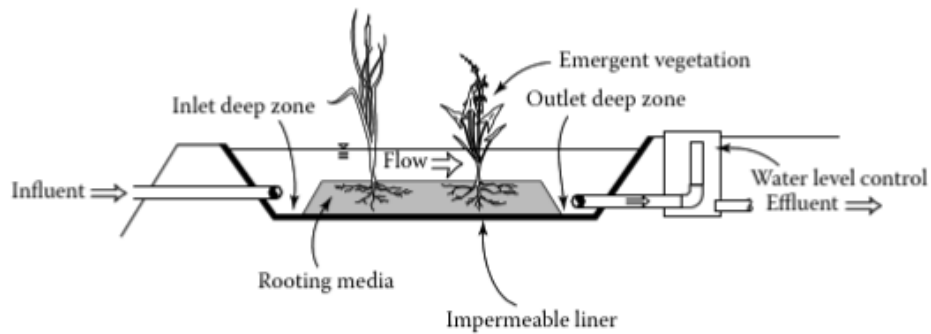


Figure 2-6 Illustration showing the basic elements of a FWS wetland (Robert H. Kadlec et al., 2008).

FWS treatment marshes are competitive when it comes to construction and operational cost relative to alternative technologies (Robert H. Kadlec et al., 2008).

HSSF wetlands (Figure 2-7) are designed to treat primary effluent before discharge as surface water or soil dispersal. The configuration is normally used in secondary treatment for smaller communities (Cooper, Job, & Green, 1996), small cluster systems and single-family houses (Wallace & Knight, 2006). Wastewater flows around the plant's roots and rhizomes, intending to flow underneath the surface of constructed wetland media. HSSF systems are more expensive compared to FWS. However, as FWS wetlands, HSSF wetlands do also serve low cost regarding maintenance compared to alternative technologies. Due to the opportunity for insulation of the top, these systems can be suited for operation under colder conditions than FWS. For smaller flowrates, HSSF are chosen rather than FWS due to space and cost (Robert H. Kadlec et al., 2008).

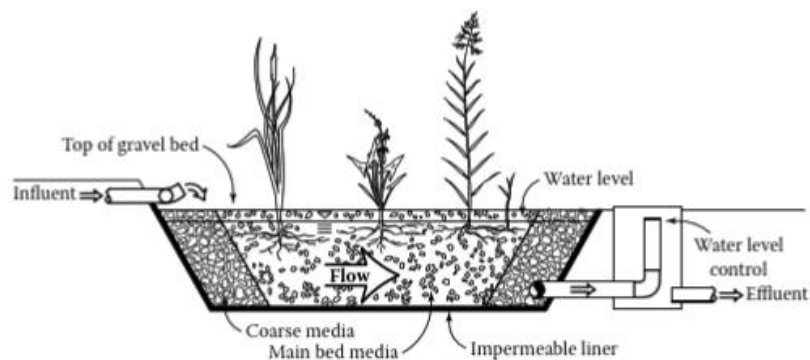


Figure 2-7 Illustration of a HSSF wetland.(Robert H. Kadlec et al., 2008)

In Europe, the most common version of VF wetlands is a single-pass configuration with surface flooding of the bed (Figure 2-8) (Normungsinstitut, 2005). They were developed with the intention to increase the level of oxygen transfer and may be combined with FWS and HSSF wetlands to create nitrification-denitrification treatment trains. VF wetlands are used in treatment processes to treat high-level ammonia waste, such as food processing wastewaters and landfill leachates due to the ability to produce nitrified effluent (Burgoon, Kadlec, & Henderson, 1999). Another application of the VF systems is to create anaerobic conditions in the bottom bed sediments where overlying water block the oxygen pathway down. VF systems can also operate with highly concentrated wastewater (Robert H. Kadlec et al., 2008).

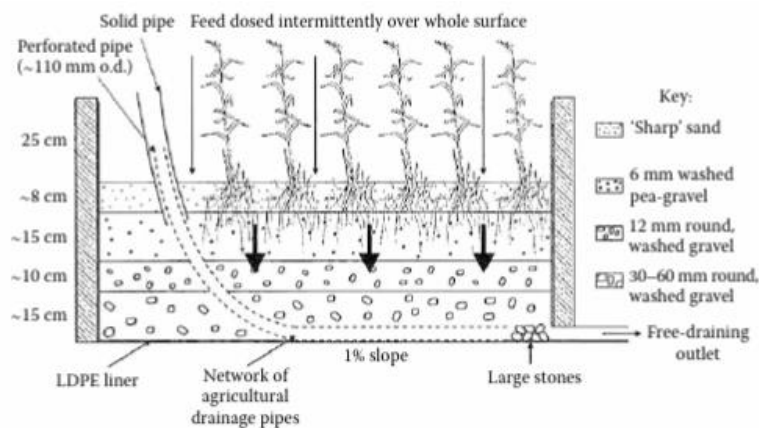


Figure 2-8 Illustration showing a typical arrangement of a VF constructed wetland (Robert H. Kadlec et al., 2008).

2.5.2 Constructed wetland biogeochemistry

All biological processes in wetlands are affected by the physical and chemical environment. The four most important abiotic factors are dissolved oxygen, oxidation-reduction potential, pH, and alkalinity (Robert H. Kadlec et al., 2008). Rivers and streams usually have a high content of oxygen. However, water added a considerable amount of organic matter from agriculture and sewage from households lower the amount of oxygen in streams with weak current. Oxygen consumption by microorganisms break down organic matter (Økland, 1998). In FWS wetlands oxygen transfer is commonly due to underwater photosynthetic production and interfacial aeration. The gradient of oxygen is reflected by various oxidation steps and the present chemical compounds (Figure 2-9).

Oxygen is an essential factor for the growth of animals and plants present in the wetland. Plants have physiological adaptations that allow growth in soil with low oxygen level, while nitrification of organic compounds are dependent on dissolved oxygen. Although the soil contains close to zero concentration of free oxygen, it still supports different oxidation and reduction reactions such as the conversion of ferric-ferrous iron (Robert H. Kadlec et al., 2008). pH is an important factor in biochemical transformations and controls the solubility of gases and solids in the water. In wetlands, photosynthesis and the input of CO₂ saturated water can

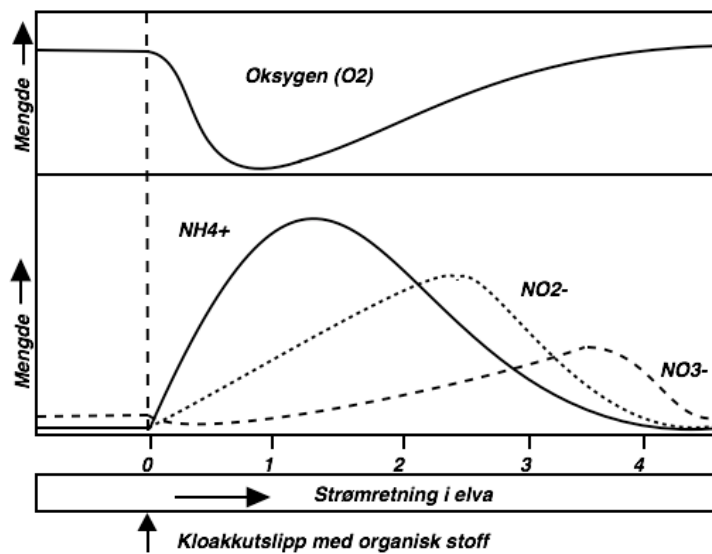


Figure 2-9 Illustration of the amount of oxygen as a function of nitrogen compounds in water added sewage from households. Modified from (Økland, 1998).

cause a shift in pH. Photosynthesis shift the carbonate-bicarbonate-carbon dioxide equilibrium to a higher pH by the utilization and production of carbon dioxide and oxygen, respectively (R.H. Kadlec, Wallace, & Knight, 1995). The operation window for many treatment bacteria is within $4.0 < \text{pH} < 9.0$, and are not able to exist outside this range (Tchobanoglous & Burton, 1991). Denitrifiers are most efficient in the range $6.5 < \text{pH} < 7.5$ while nitrifiers at $\text{pH} > 7.5$. Ammonium converts to free ammonia at $\text{pH} > 7.5$ and higher temperatures. Furthermore, the hydrogen ions are active with wetland soil and sediments through cation exchange processes, which in turn determine the extent of metal bindings (Robert H. Kadlec et al., 2008).

Alkalinity is primarily the function of carbonate, bicarbonate and hydroxide content (Clesceri et al., 1998) thereby fundamental for wetland vegetation and the carbon source for autotrophic microbes (Robert H. Kadlec et al., 2008). The total alkalinity for pure water ranges from

approximately 100 mg/l to higher values in landfill leaches exceeding 400 mg/L. FWS wetlands usually reduce the alkalinity slightly (Robert H. Kadlec et al., 2008).

2.6 Nitrogen storages in constructed wetlands

The nitrogen cycle in wetlands is complex. To understand the nitrogen fluxes in a wetland, it is important to have an overview of the different nitrogen storages and their sizes (Figure 2-10). Ammonium (NH_4^+), nitrite (NO_2^-), nitrate (NO_3^-) are considered the most important inorganic forms of nitrogen in wetlands (Vymazal, 2007). However, nitrite is chemical unstable because of intermediate energetic condition, therefore found in very low concentrations. In FWS wetlands, nitrogen may also be present in organic forms, in addition to exist in dissolved and particulate forms. Usually, there are small amounts of particulate nitrogen in constructed wetlands as the main fraction of nitrogen is nitrate, which is highly soluble (Robert H. Kadlec et al., 2008).

The mass of nitrogen storages varies in the different types of constructed wetlands. Organic nitrogen compounds account for a significant fraction of dry weight in soil, microbes and plants. Runoff entering a wetland system may contain considerable quantities of inorganic solids from watershed erosion (Robert H. Kadlec et al., 2008). Compared to natural wetlands are constructed wetlands often more nutrient-enriched, therefore containing higher tissue nutrient values. Fertilization effluent increases the total biomass in the wetland as it increases the nutrient content, hence result in large storages in constructed wetlands compared to areas not exposed to fertilization.

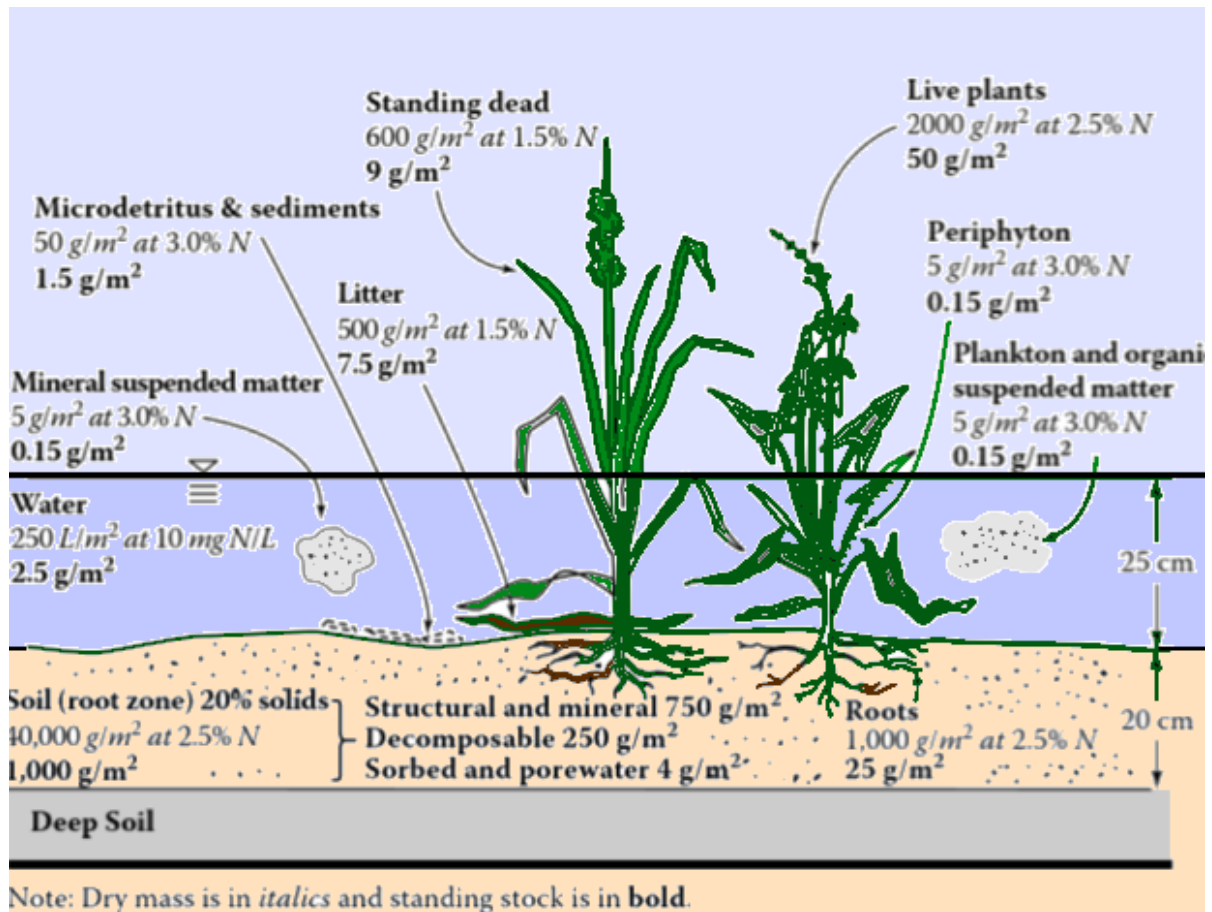


Figure 2-10 Nitrogen storages in a vegetated hypothetical FWS treatment wetland. An important notation is the amount stored nitrogen in soils and sediments ($\approx 1000 \text{ gN/m}^2$), in plant materials ($\approx 100 \text{ gN/m}^2$) and in mobile forms in the water column ($\approx 5 \text{ gN/m}^2$) Modified from (Robert H. Kadlec et al., 2008).

Seasonal varieties of temperature influence TN concentration in biomass. Studies have observed lower nitrogen content in biomass collected at the end of growing seasons than in the spring, partly due to translocation to belowground rhizomes (Kühl & Kohl, 1993).

2.7 Main removal and retention mechanisms of nitrogen in constructed wetlands

The main removal mechanisms for nitrogen in constructed wetlands are ammonification subsequent nitrification-denitrification (dissimilation), plant uptake (assimilation) and removal through harvesting of biomass (Langergraber et al., 2017; Maltais-Landry et al., 2009; Xie, Chen, & You, 2018). Different forms of nitrogen are continuously involved in chemical transformations between organic and inorganic compounds (Figure 2-11). Processes

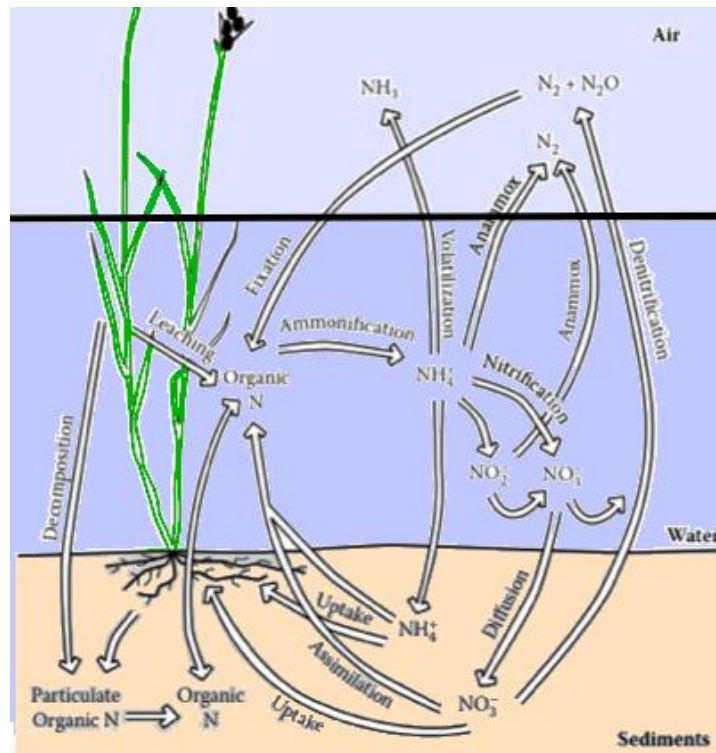


Figure 2-11 The nitrogen cycle in a FWS wetland. Modified from (Robert H. Kadlec et al., 2008)

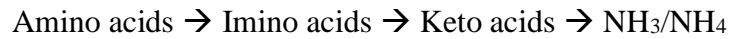
transferring nitrogen compounds in wetlands can be divided into physical and chemical processes. Physical processes include atmospheric deposition, particle settling and resuspension, diffusion of dissolved form, litter fall, ammonia volatilization, sorption of soluble nitrogen on substrates and plant translocation. Chemical processes include ammonification, nitrification, denitrification, assimilation and decomposition (Robert H. Kadlec et al., 2008). All pathways in the nitrogen cycle are active in constructed wetlands. However, it is believed that only some of them contribute significantly to removal mechanisms and nitrogen transformations in wastewater treatment (Langergraber et al., 2017).

2.7.1 Ammonification subsequent nitrification-denitrification

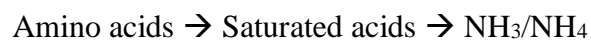
Ammonification (mineralization) is the biological process where organic nitrogen is converted into ammonia or ammonium through extracellular activity (Langergraber et al., 2017). In constructed wetlands receiving influent rich on organic nitrogen, this process is considered the first step of nitrogen transformation (Xie et al., 2018). However, it is seldom a limiting step for the removal of total nitrogen. The rate of ammonification process are faster in oxygenated zones compared to less oxygen containing environment (Lee et al., 2009; Vymazal, 2007).

Temperature, pH, available nutrients, C/N-ratio and soil structure are factors influencing the rate. The optimal temperature and pH for ammonification process are reported to 40-60 °C and pH 6.5-7.5 (Vymazal, 2007). Ammonification is a process essentially a catabolism of amino acids, including several types of deamination reactions (Equation 1 and Equation 2).

Equation 1 The oxidative deamination of ammonification process



Equation 2 The reductive deamination of ammonification process



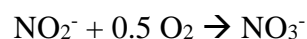
The equilibrium between ammonia (NH₃) and ammonium (NH₄⁺) in water is a pH dependent equilibrium (Equation 3) influenced by ionic strength and temperature (Vymazal, 2007). In general, in water with pH neutral and lower at room temperature are the proportion of ammonia-N considered very-very low while ammonium-N is considered very-very high (Hach, 2019).

Equation 3 The chemical equilibrium between ammonia and ammonium



Nitrification is defined as a biological oxidation of ammonium to nitrate, with nitrite as an intermediate in the sequence of reaction (Equation 4) (Vymazal, 2007). Nitrification is a slower process compared to ammonification (Lee et al., 2009).

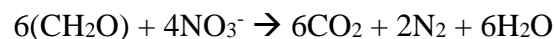
Equation 4 The process of nitrification



The nitrification process is a two-step process performed by different bacterial genera (most commonly) *Nitrosomonas* and *Nitrobacter*, using ammonia or nitrite as energy source. Oxygen serves as the electron acceptor and carbon dioxide the carbon source (Lee et al., 2009). For nitrification to take place, oxygen, alkalinity, micronutrients and microorganisms must be present in the water (Langergraber et al., 2017). The optimal temperature and pH are approximately 25-30 °C and 6.6-8, respectively. With a minimum of 4-5°C which is minimum temperature for bacterial growth of *Nitrosomonas* and *Nitrobacter* (Vymazal, 2007). Nitrification does not result in nitrogen removal, unless coupled to denitrification.

Denitrification is defined as the process where nitrate is converted into dinitrogen via nitrite, nitric oxide and nitrous oxide as intermediates (Vymazal, 2007) in anaerobic and anoxic environments (Widowati, S., & R., 2018) (Equation 5). As denitrification process converts nitrate to nitrogen gas released to the atmosphere, it is considered a vital process for effective nitrogen removal (Langergraber et al., 2017).

Equation 5 The process of denitrification



Denitrification can be difficult to achieve in most wastewater treatment systems as nitrification is a prerequisite for ammonia-nitrate conversions. Nitrification takes place when sufficient organic carbon is consumed which may result in limited amount of organic matter residual for denitrification (Langergraber et al., 2017). Removal of total nitrogen by denitrification is typically 60-95% compared to assimilation by plants and algae with a removal of 1-35%. Microsites with steep oxygen gradients are believed to be established in constructed wetlands, allowing nitrification and denitrification to occur in sequence. The electron donor for nitrate reduction, organic carbon, provides an energy source for organisms performing denitrification (Lee et al., 2009). Denitrification is influenced by the pH, temperature, nitrate concentration, microbial flora, the carbon source, absence of oxygen, presence of denitrifiers, water level, soil type, hydroperiods, redox potential and overlaying water (Vymazal, 2007).

Ammonium is a cation and can be immobilized through ion exchange onto negatively charged soil particles (Mitsch, 2015). The sorption capacity is controlled by the chemical composition and particle size of media, being lower for sand and gravel particles due to the available surface area per unit volume. Sorption of ammonium are considered a minor retention mechanism of

nitrogen compounds. However, sorption may aid the nitrification-denitrification in constructed wetlands that are storing ammonium temporarily. Temporarily stored ammonium allows heterotrophs to consume organic matter before exposing the ammonium sorbed onto particles to oxygen, resulting in nitrification. Further, denitrification takes place after nitrate reacts with organic matter. The sorption site is then restored for a new ammonium molecule. This mechanism is dependent on very low loading rates or if very high sorptive capacities dominate (Langergraber et al., 2017).

2.7.2 Plant uptake and harvesting

Assimilation is the conversion of inorganic nitrogen forms into organic compounds, through macrophyte growth, microorganisms and algae. Assimilation of nutrients from sediments are performed by emergent macrophytes, while assimilation of nutrients from water are performed by floating macrophytes (Vymazal, 2007). Emergent macrophytes do store nitrogen, using organic compounds as building blocks for tissues and cells. Ammonia and nitrate are the two forms of nitrogen most active in assimilation, depending on the environment. A misconception of nitrogen removal in constructed wetlands is that most of the nitrogen is removed by plant uptake. Nutrient uptake by plants is limited by the concentration of nutrients in plant tissue and its net productivity (Vymazal, 2007). Depending on the macrophyte species considered may nitrogen removal by plant uptake range from 100-250 gN/m²*year by floating large-leaved plants and 50-150 gN/m²*year for floating small-leaved plants (Robert H. Kadlec et al., 2008). Desirable plant traits used for assimilation and storage include high tissue nutrient content, rapid growth and the crop's ability to stand high (Vymazal, 2007).

Regularly harvesting of biomass above ground can remove some of the nitrogen stored in plants. However, more than half of the nitrogen is stored below ground in tissue. Translocation of nitrogen between below and above ground depends on the season. Therefore, timing of harvesting is important. How effective harvesting of biomass is regarding nitrogen removal is varying, depending on the amount of nitrogen in the system and operational cost of removal. However, if biomass is not harvested will nitrogen in tissue be released during decomposition of the plant matter, resulting in no net nitrogen removal (Robert H. Kadlec et al., 2008; Langergraber et al., 2017).

2.8 Objectives of thesis

The main objective of this thesis is to monitor a mature constructed wetland, Leikvollbekken, with respect to nitrogen retention. The constructed wetland was initially designed to remove nitrogen and phosphorus in agricultural runoff before reaching Store Stokkavatn but has had little maintenance in the recent years. Previous thesis's estimated the total phosphorus retention in the wetland to 31% in the period from July 2016- June 2017 (Krahner, 2017) and 7% in the period from August 2017 -May 2018 (Luth-Hanssen, 2018). No previous results on long-term retention efficiency of nitrogen compounds have been found on this site. However, the hypothesis was that a positive retention of nitrogen compounds will occur through biological nitrogen assimilation and dissimilation. Monitoring of nitrogen retention in mature constructed wetlands are important for future design and measures for treating agricultural and urban runoff.

The monitoring was achieved by collecting weekly water samples. In addition, a storm event was included to investigate the constructed wetland's effect on parameters under high hydraulic input. The weekly water samples were analyzed for NO_3^- , NH_4^+ , soluble TN, TN. In addition, TSS, pH, alkalinity, conductivity and color were measured to investigate if any connection with nitrogen compounds existed.

3. Methods

This section describes the site monitored during the thesis, precipitation and temperature data, sampling procedures as well as the quantitative analytical methods used. Once a week composite water samples were collected in Leikvollbekken and analyzed at the laboratories at the University of Stavanger. Weekly water samples were analyzed for NO_3^- , NH_4^+ , TN, TSS, FSS, pH, conductivity, alkalinity and color. Additional samples from Store Stokkavatnet, Madlabekken, and samples collected during a storm event were included.

Two different methods were used to measure nitrate, Spectroquant Cell Test on weekly water samples, and ISE Nitrate Electrode on storm event samples. Due to large discrepancies between measured values, other methods were introduced for comparison.

3.1 Site description

Leikvollparken is one of four constructed wetlands established next to Litle- and Store Stokkavatn by Stavanger Municipality. It was built in 1993/94 (Figure 3-1) and is classified as a mature constructed wetland (Stavanger Municipality, 2019).

The tributaries to Store Stokkavatn influences the water quality of what is currently one of the emergency water supply in the Jær region (IVAR.no, 2019). The lake is surrounded by agricultural areas, residential fields and roads releasing nutrients and pollution; areas which previously consisted of streams, wetlands and marshy terrain (Figure 3-2). As the nature's own cleaning systems are replaced with urban areas, pollution is not retained by plants and soil as before. The main challenge with Leikvollbekken prior to the construction of the wetland was the high transportation of pollution to Store Stokkavatnet. The supply of soil and livestock manure through flood peaks and erosion episodes was thought to be the source of problems (Bakke, 1993). The typical concentration of total nitrogen was 11 mg/L with large variations over time (Løvhøyden, 1994). Expected concentration of NH_4^+ in the outlet of CW was set to less than 1 mg/L, while the transportation of nitrogen was expected to be reduced by 2000 kg/year (Bakke, 1993).

Leikvollbekken and the additional four constructed wetlands, are designed with the intention of recreating the same cleaning effect that natural wetlands would perform (Stavanger Municipality, 2019). Furthermore, the constructed wetland has a positive effect for the



Figure 3-1 Picture of the sampling house at Leikvollbekken in 1993/1994 and 2019, respectively, showing the location of V-notch in front of the house. Picture from 1993/1994 is provided by Espen Enge (UiS), picture from 2019 is taken 6th of May 2019.

diversity of nature and was built with an emphasis on an ecological interaction between the treatment plant, Store Stokkavatn and surrounding area (Stavanger Municipality, 1993).

Leikvollbekken was constructed as an extensive biological wastewater treatment plant consisting of various technical cleaning processes combined together with the purpose of purify the contaminated pelvis. In the design, emphasis has been placed on obtaining efficient cleaning of phosphorus (mainly) and nitrogen by creating an ecosystem where the processes of self-cleaning are reinforced. A combination of suited bacteria, algae, plant and animal cultures was introduced to a plant consisting of ponds, open channels and permeable dams. Nitrogen removal would go through biological assimilation and dissimilation (Stavanger Municipality, 1993).

Pond 1 and Pond 2 was estimated to 733 m² and 633 m², respectively (Kartdata: Geovekst, 2019). An illustration of the constructed wetland design is presented in Figure 3-3. The information board (Appendix I) at site shows a more detailed illustration of the original design concept. Pond 1 consist of a deep zone after the first permeable dam for particle settlement. Plants in the ponds disperse the water and act as habitat for bacteria and organisms.



Figure 3-2 To the left: Map over the area surrounding Store Stokkavatn and Leikvollbekken. Agricultural areas are marked in yellow, urban areas are marked in red, forest areas are marked in green and scanty vegetation areas are marked in grey (Kartdata: Geovekst, 2019). To the right: Illustration of the watershed of Store Stokkavatn (Geodata AS).

The dams regulate the water level and disperse water over larger area. Moreover, a deeper zone for particle settlement is located between dam 3 and 4. Several areas of the constructed wetland do today consist of dense vegetation and sediment loads, resulting in less spread water and a clear channel in Pond 1 (Figure 3-4). The channel was created a few years ago, leading the water straight through the first pond due to accumulation of water on the upside of the treatment plant at agricultural soil (Kristin Herdis Bringedal, pers. comm.)

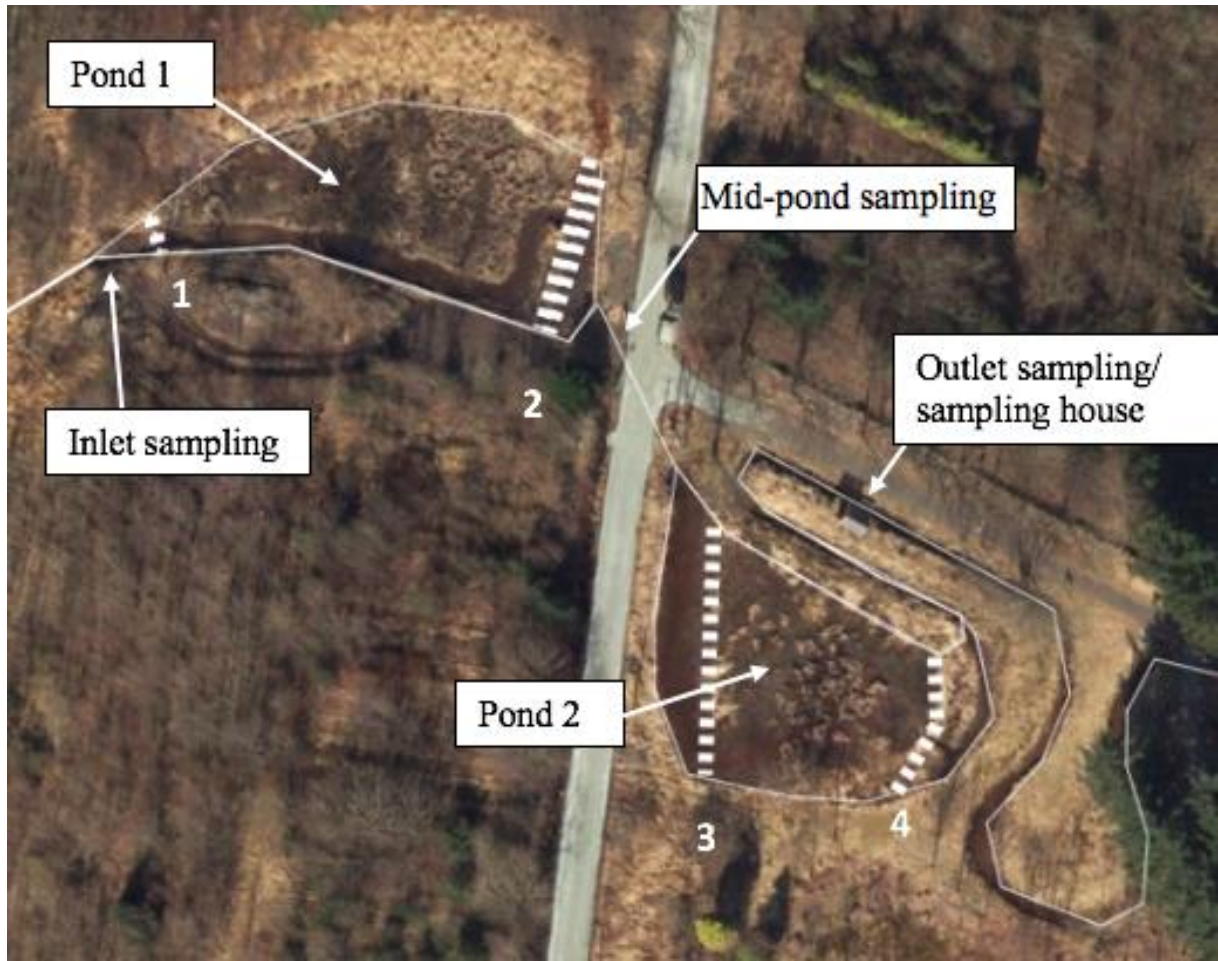


Figure 3-3 Illustration of Leikvollbekken today with endorsed original dams (1-4) inspired by the information board at site. 1:625 (Kartdata: Geovekst, 2019).



Figure 3-4 Picture of Pond 1. Notice the "oily" surface to the right (13.02.2019).



Figure 3-5 Picture of Pond 2. (13.02.2019)

3.2 Precipitation and temperature data

Daily precipitation and temperature data were obtained from the closest measuring station “Våland målestasjon” in Stavanger Municipality. The measuring station is located at 72 m.a.s.l (Meteorologisk institutt, 2007-2019) approximately 4.1 km from Leikvollbekken (Kartverket, 2019). Precipitation data from 1st of October 2018 to 13th of May 2019 is presented in Figure 3-6, including highest, lowest and mean temperature for the period. The captured storm event is highlighted and more detailed presented in Figure 3-7. Monthly weather data for the study period and more detailed precipitation data for storm event are presented in Appendix C.

Maximum monthly precipitation at 275.7 mm was observed in October with the highest peak of 60.8 mm/d. The month with least precipitation was April with a total of 43.8 mm (May was not considered due to only 13 days of data). October and April had the highest average temperature while January was coldest. The average temperature decreased from mid-October to beginning of January, then started to slowly increase up to approximately the same highest average temperature in the end of April, in a fluctuating pattern (Figure 3-6).

The storm event studied was monitored 24 hours from 18:00 the 26th of April 2019. A 23-day period without precipitation occurred before the storm, except for approximately 2.1 mm precipitation the day before (Meteorologisk institutt, 2007-2019). In this period, increasing temperature was observed (Figure 3-6). The total accumulated precipitation during the storm was 40.4 mm, with an average precipitation rate of 1.7 mm/h. The storm event consisted of

three main peaks, 4.1 mm at 19:00, 3.3 mm at 03:00 and 2.4 mm at 09:00, respectively. Several sub-peaks are observed around peak two and three.

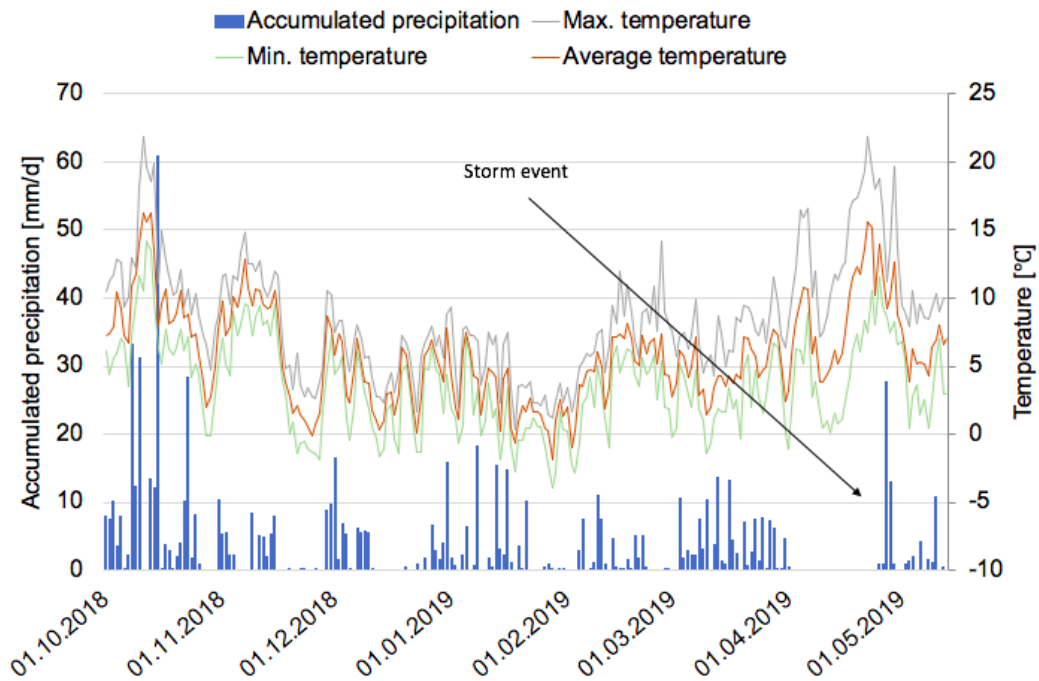


Figure 3-6 Daily accumulated precipitation and temperature measurements at Våland weather station during the period 1st of October 2018 to 13th of May 2019 (Meteorologisk institutt, 2007-2019)

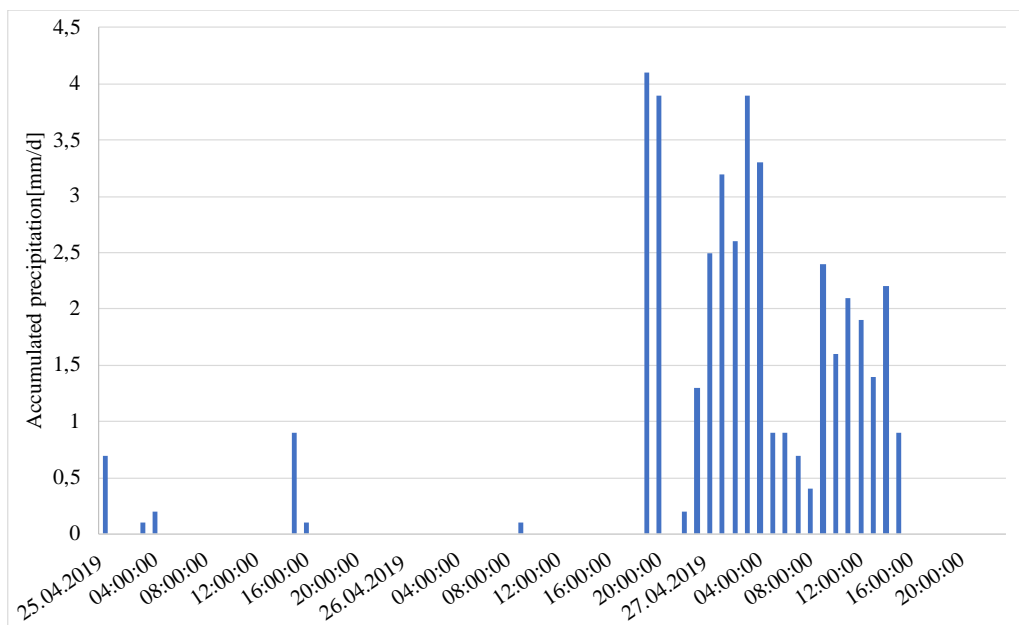


Figure 3-7 Accumulated precipitation from Våland weather station from 25th-27th of April 2019 (Meteorologisk institutt, 2007-2019).

3.3 Sampling procedures during weekly water samples and storm event

Water samples were collected approximately once a week from 1st of October 2018 to 13th of May 2019. Inlet sampler was first installed seven weeks into the sampling period. Problems with mid-sampler occurred and led to no midstream samples taken in the period 4th of December 2018 until 10th of April. From 15th-29th of November 2018 no sample was taken due to frost in Leikvollbekken and problems with the sampling equipment.

3.3.1 Inlet samples

Inlet samples were taken by a time-proportional ISCO 6712 Full-size Portable Sampler placed above the inlet to pond 1 (Figure 3-8) equipped with a 10 L container (Figure 3-9). The sampler was programmed to take a 70 ml sample every 1-1.5 hour depending on the amount of days.



Figure 3-8 To the left: Red arrows point at the sampling equipment and the suction tube. To the right: The suction tube from another viewpoint. The oily surface was also observed 27th of February (13.04.2019).



Figure 3-9 To the left: The automatic sampler connected to a car battery for power supply. To the right: The inside of the sampler showing the sample container during weekly water sampling. (06.02.19)

3.3.2 Mid-pond and outlet samples

Mid-pond and outlet samples (Figure 3-3) were taken by two ISCO 6712 Full-Size Portable Samplers (Figure 3-10). The samplers were programmed to take flow-proportional samples. Depending on the water level, the samplers were set to sample 50 ml every 10 pulses in periods with high flow and 7-8 in periods with low flow.

The samplers were equipped with a 11L containers each stored in a refrigerator. Sample containers were cleaned regularly to ensure removal of remaining organic material. The mid-sampler failed in the period 4th of December 2018 to 10th of April due to lack of response to pulses transmitted from flowmeter. From 4th of April this sampler was reprogrammed to take time-proportional samples instead of flow-proportional.



Figure 3-10 The ISCO 6712 Full-Size Portable samplers for inlet and outlet of Pond 2 connected to a container inside a refrigerator, placed inside the red sampling house. The picture to the right shows the flowmeter registering the flow data and transmitting pulses to the samplers. (13.05.19)

During the storm event were the three ISCO 6712 Full-Size Portable Samplers programmed to take time-proportional samples. The containers were replaced with a 24-bottle carousel, each bottle 1L. The mid-pond sampler had 23 bottles. An ice pack was added to each carousel to ensure cold samples. Every 15 minute a sample of 200 ml was taken, 4 samples in each bottle. The 24 hours prior to the storm event was sampled with composite samples from 12 hours.

3.3.3 Reference samples

In addition to inlet-, mid-pond- and outlet samples from Leikvollbekken, additional samples were taken in two different locations every week in the period 17th of January to 17th of April 2019. Manually sampling was performed north of Leikvollbekken outlet in Store Stokkavatn and in Madlabekken (Figure 3-11). It is important to notice that Reference point 1 was taken from quiescent water area, while Reference point 2 was taken in flowing water. The reference samples were taken to compare recipient concentrations with the concentrations in Leikvollbekken.

A grab sample from the “oily” surface (Figure 3-4) was taken to investigate if any of the parameters significantly differed from the other measuring locations.



Figure 3-11 Additional samples were taken at Reference point 1 (Store Stokkavatn) and Reference point 2 (Madlabekken).

3.3.4 Flow measurements

Flow measurements were carried out using a Teledyne ISCO Signature Flow Meter (Figure 3-10) registering flow data every 15 minutes in inlet and outlet of Pond 2.

A TIENet 350 Area Velocity Sensor is positioned inside the fully submerged pipeline connecting Pond 1 and Pond 2 mounted in the bottom of the channel (Kommedal, R. pers. comm). The sensor is measuring the average velocity in the pipe using continuous ultrasonic sound waves that detects particles. Periods with low particle concentrations may result in inaccurate flow registering. The Signature Flow Meter calculates the flow rate and total flow using the measured average velocity combined with the known fixed pipeline area (TELEDYNE ISCO Signature Flow Meter 2013).

Outlet flow is measured by an ISCO TIENet 330 Bubbler placed with the sampling house upstream of the v-notch (Figure 3-1). The ISCO TIENet 330 Bubbler consist of a pressure transducer sensing the pressure required to form bubbles from the end of the submerged bubble line, which in turn is directly dependent on the hydrostatic pressure caused by the liquid level in the open channel. The flow meter receives a level signal converted from pressure measured by the bubbler module to calculate the flow rate and total flow (TELEDYNE ISCO Signature Flow Meter 2013). Data reports from Teledyne ISCO Signature Flow Meter were processed in Flowlink 5.1 Software before used in the thesis.

Sediment settling and plant bloom in the submerged pipeline connecting Pond 1 and Pond 2, combined with periods with low particle concentrations reduces TIENet 350 Area Velocity Sensor’s reliability. The probe used to measure outlet flowrates are considered better quality, thus more precise and used further in results and discussion.

3.4 Analytical methods

The ten parameters measured during the laboratory work are shown graphically in Figure 3-12 and further described in following subsections. Chemicals and solutions used in the analysis, their quality and producers, and their purpose are listed in Appendix A.

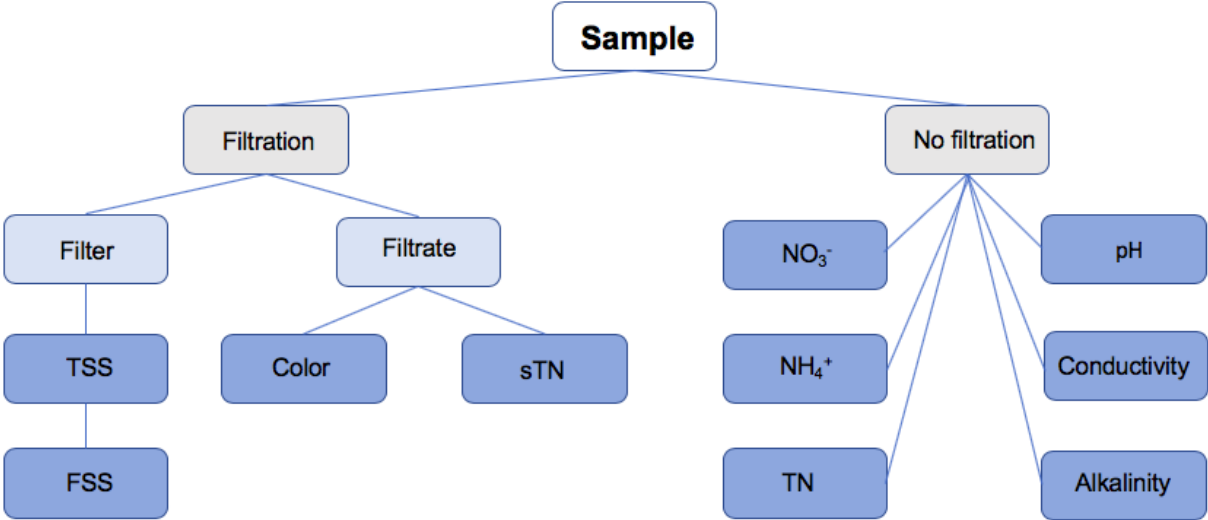


Figure 3-12 An overview of parameters measured during laboratory work, represented in blue boxes.

3.4.1 Nitrogen parameters

NO_3^- , NH_4^+ and TN were measured during the entire sampling period, with some exceptions. Two methods were used to measure NO_3^- : Spectroquant Cell Tests in weekly water samples and Ion-Selective Electrode in storm event samples. Large differences in concentration between the methods were observed. Due to this, additional methods were included for comparison purposes. The results and evaluation of this is presented as a separate subsection in its respective part of the thesis.

Nitrate

The two main methods for nitrate analysis used included Spectroquant Cell Tests and Ion-Selective Electrode. From 1st of October 2018 to 10th of January were measured values directly read from preset method calibration. From 17th of January 2019 were NO_3^- -N and TN concentrations calculated from calibration curves (Appendix B). A calibration curve was made for each analysis based on standard solutions at 1, 5 and 10 mg/L NO_3^- -N diluted from a stock solution at 100 mg/L.

Spectroquant Nitrate Test 14563 and 09713

Nitrate concentration in samples were determined using Merck Spectroquant Nitrate Test 09713 and 14563. Nitrate reacts with 2,6-dimethylphenol to form 4-nitro-2,6 dimethylphenol in sulfuric and phosphoric solution. The 4-nitro-2,6-dimethylphenol in solution is determined photometrically. Samples were measured in Merck Spectroquant Pharo 300 photometer directly in reaction cell or by using 10 mm cuvettes at preset absorbance wavelength (Spectroquant, 2009). Test 14563 had a measurement range of 0.5-25 mg/l NO_3^- -N and Test 09713 of 1.0-25.0 mg/l NO_3^- -N. Test 14563 is by the manufacturer reported to have a standard error/deviation of ± 0.13 mg/l NO_3^- -N and 09713 of ± 0.10 mg/l NO_3^- -N.

Ion-Selective Electrode with and without AgSO_4 :

Nitrate were measured using ISE25 NO_3 Nitrate Electrode (Radiometer Analytical), an equipment used for direct measurement of nitrate ions in aquatic solutions. ISE25 NO_3 is a PVC membrane electrode with a nitrate ion carrier. 10 ml ionic strength adjustor (ISA) 0.2 M

$\text{KH}_2\text{PO}_4 + \text{NO}_3\text{-N}$ 0.25 mg/l were added to 10 ml sample. ISA correct the activity and concentration difference in the samples and calibration samples as they must be of equal ionic strength. 0.25 mg/l nitrate was added to the solution to prevent measurements under the detection limit. The value was subtracted from the final concentration.

Same procedure was done by adding 0.5 ml AgSO_4 to all samples to reduce the interference of ions. Silver sulfate was added to precipitate Cl^- as AgCl .

The standard addition technique:

The potential (E) of a sample were measured using ISE25 NO_3 Nitrate Electrode. 1 ml of 100 mg/l NO_3^- -N solution was added to a 10 ml water sample and 10 ml ISA. The potential (E_1) was then measured and calculated nitrate concentration was calculated from Equation 6.

Equation 6 The standard addition technique

$$C_{smp} = \pm \frac{C_{std} + V_{std}}{(V_{smp} + V_{std}) * 10^{\frac{[E_1 - E]}{s}} - V_{smp}}$$

Where:

C_{smp} : Concentration of NO_3^- -N in sample [mg/L]

C_{std} : Concentration of NO_3^- in standard [mg/L]

V_{smp} : Sample volume [ml]

V_{std} : Total volume of standard added [ml]

E: Potential measured before first addition/subtraction [mV]

E_1 : Potential measured after addition/subtraction [mV]

S: Electrode sensitivity [mV/pC]

The standard addition technique (Mikhelson, 2013) is suitable for analyzing samples in which interferences and the ionic strength are moderate to high variable. Samples were assumed to contain elements causing interferences in the results. This method was also tested with 1 ml added silver sulfate.

The Zinc reduction method

Nitrate concentration was determined according to slightly modified Standard methods 4500 E (Eaton, Clesceri, & Greenberg, 1995). Cadmium was replaced with Zinc due to its environmental toxicity, as they have close to the same properties. NO_3^- is reduced to NO_2^- in the presence of zinc and is further diazotized with sulfanilamide and coupled with N-(1-naphthyl)-ethylenediamine dihydrochloride. The colored azo dye was measured colorimetrically in a Shimadzu UV-120-01 spectrophotometer at 550 nm in 4 cm cuvette. As the applicable range is 0.01-1 mg/L NO_3^- /L were the original samples diluted 1/10. The unknown concentration of the samples was determined from a calibration curve based on 0.1, 0.2, 0.4 and 0.75 mg NO_3^- /L standard solutions.

Ammonium

NH_4^+ concentrations were determined using Spectroquant Ammonium Test 14752 and 14739. Ammonium occurs partly as ammonia and partly in the form of ammonium ions, containing a pH-dependent equilibrium. The ammonia forms monochloramine by reacting with a chlorinating agent. Furthermore, it reacts with thymol and creates a blue indophenol derivate which in turn is determined photometrically. The measurement solution is yellow-green to green in color due to the reagent blank's intrinsic yellow coloration. Samples were measured in Merck Spectroquant Pharo 300 photometer directly in reaction cell or by using 10 mm cuvettes at preset absorbance wavelength depending on what type of Cell Tests used (Spectroquant, 2009). Test 14739 had a measurement range in between 0.010-2.000 mg/l NH_4 -N and Test 14752 0.05-3.00 mg/l NH_4 -N. The Spectroquant Ammonium Test 14739 is by the manufacturer reported to have a standard error/deviation of ± 0.013 mg/l NH_4 -N and Test 14752 of ± 0.021 mg/l NH_4 -N.

Total nitrogen

Total nitrogen was determined with Merck Spectroquant Total Nitrogen Test 14537 in the period 5th of November 2018 to 10th of January 2019. From 17th of January 2019 to 13th of May 2019 analysis were performed using digested samples in Spectroquant Nitrate Test 09713. Acid digestion was performed according to the Standard Methods 4500 D "Persulfate method" (Eaton et al., 1995). Nitrogen compounds oxidize to NO_3^- by adding 5 ml alkaline digestion

reagent before treated in an autoclave for 30 min. at 110 °C. 1 ml borate buffer solution was added to sample before measured in Merck Spectroquant Pharo 300 photometer directly in reaction cell or by using 10 mm cuvettes at preset absorbance wavelength (Spectroquant, 2009). In addition to raw samples, soluble nitrogen was determined by analyzing total nitrogen in samples filtered through 0.7 μm Whatman GE Healthcare Life Science glass microfiber filters (55 mm). Particulate nitrogen was calculated by subtracting soluble nitrogen from total nitrogen.

3.4.2 Total suspended solids and Fixed suspended solids

TSS and FSS were determined according to Standard Methods 2540 D and 2540 E by drying, combustion and weighing (Clesceri et al., 1998). Adequately sized Whatman GE Healthcare Life Science 1.2 μm glass microfiber filters (55 mm) were placed in a drying oven (Termaks TS 9135) to ensure completely dry filters before use. TSS was obtained from filtration of well-composite samples. Retained residue on filter paper was dried to a constant weight at 103-105 °C, before cooled in desiccator. FSS was calculated from the TSS residue ignited at 550 °C in a Nabertherm B170 muffle furnace for 30 minutes followed by cooling to room temperature. An additional clean filter paper was carried through FSS procedure to note the loss of filter mass in the muffle furnace. All filters were kept in desiccators for removal of water residue.

3.4.3 pH

pH was determined according to Standard Method 4500-H A digital pH-meter Mettler Toledo with Radiometer GK2401c electrode was used. The pH-meter was calibrated using standard buffers at pH 4.01 and 7.00. For measurements in water under normal conditions, the limit of accuracy is ± 0.1 pH units (Eaton et al., 1995).

3.4.4 Alkalinity

Alkalinity was determined by titrating water samples with 0.01 N H_2SO_4 . pH was measured using the digital pH-meter. By linear regression, a titration curve of $[\text{H}^+]$ vs. titrated volume was made for each sample, including the three data points exceeding equivalence point at pH

4.5. A formula to adjust over titration (Henriksen, 1982) was used to calculate the true alkalinity for all samples (Equation 7).

Equation 7 Calculation of the equivalence alkalinity

$$ALK_E = ALK_{pH=4.5} - 32 + 0.646 * \sqrt{ALK_{pH=4.5} - 32}$$

Where:

ALKE: Equivalence alkalinity [$\mu\text{mol/L}$]

ALK_{pH=4.5}: Alkalinity corresponding to an endpoint of pH=4.5 [$\mu\text{mol/L}$]

3.4.5 Conductivity

Conductivity was measured according to Standard Methods 2510 using a pHenomenal CO 3100L conductivity meter. The conductivity reflects the water's ability to conduct electrical current, which is an indirect measure of dissolved ions in the water. The manufacturer have reported an accuracy of 0.5% of measured value (VWR, 2019).

3.4.6 Color

Color was determined according to ISO 7887:2011. The intensity of the color in the sample is determined by absorption at wavelength 410 nm. The absorbance is compared to a specific absorption coefficient obtained from a comparison solution of potassium hexachloroplatinate and cobalt chloride at the same wavelength. The color produced in the comparison solution is close to the natural yellow-brownish color produced by humic substances. The absorption of a filtrated sample was measured in a 50 mm glass cuvette using Spectroquant Pharo 300 Merck spectrophotometer. The true color of a sample C in mg/l Pt was determined by Equation 8:

Equation 8 The true color of a water sample

$$C = \frac{A_{410}}{a * d}$$

Where:

C: The true color of sample [mg/l Pt]

A₄₁₀: The absorbance of the sample

a: The specific absorption coefficient for the comparison solution [mm⁻¹(mg/l Pt)⁻¹]

d: The light path to the measuring cell [mm]

3.4.7 Error analysis and statistical method

Standard deviation was performed according to Standard Methods 1020 B (Clesceri et al., 1998). Standard deviations for Spectroquant Cell Tests NO₃⁻, NH₄⁺, TN were based on three parallels for each sample from 5th of October to 13th of December 2018. The deviation for ISE measurements was calculated based on two parallels in the same period.

Statistical analysis was performed with simple regression in Microsoft Excel with a 95% confidence level. Statistical analysis was performed on weekly samples and storm event samples. Due to deviation between the two methods used for NO₃⁻, Spectroquant Cell Test and ISE Nitrate Electrode, was multiple regression analysis performed on a selection of weekly water samples.

4. Results

Results obtained during the experimental part of thesis are presented in this section, consisting of four subsections presenting the results from the long-term monitoring of Leikvollbekken, the storm event and supplementary results. An additional subsection on statistical analysis of methods used in determining nitrate concentrations is included.

The subsections “Long-term monitoring” and “Storm event” are again divided into 1) hydraulic load, 2) Variations and retention of nitrogen compounds, 3) Variations of additional parameters and 4) Error- and statistical analysis.

4.1 Long-term monitoring

The result of the long-term monitoring of Leikvollbekken in the period of 1st of October 2018 to 13th of May 2019 is presented in this section. In average, samples were taken once a week (twice a week in October) with a few exceptions due to frost and problems with the equipment.

4.1.1 Hydraulic load

The average flowrate and accumulated precipitation per weekly composite sample tend to follow a self-similar pattern (Figure 4-1). Highest average flowrate is observed in October at 49 L/s and 38 L/s for inlet and outlet of Pond 2, respectively. Several smaller peaks characterize the rest of sampling period. Inlet flow data are slightly higher than outlet flow data, except right after the peaks.

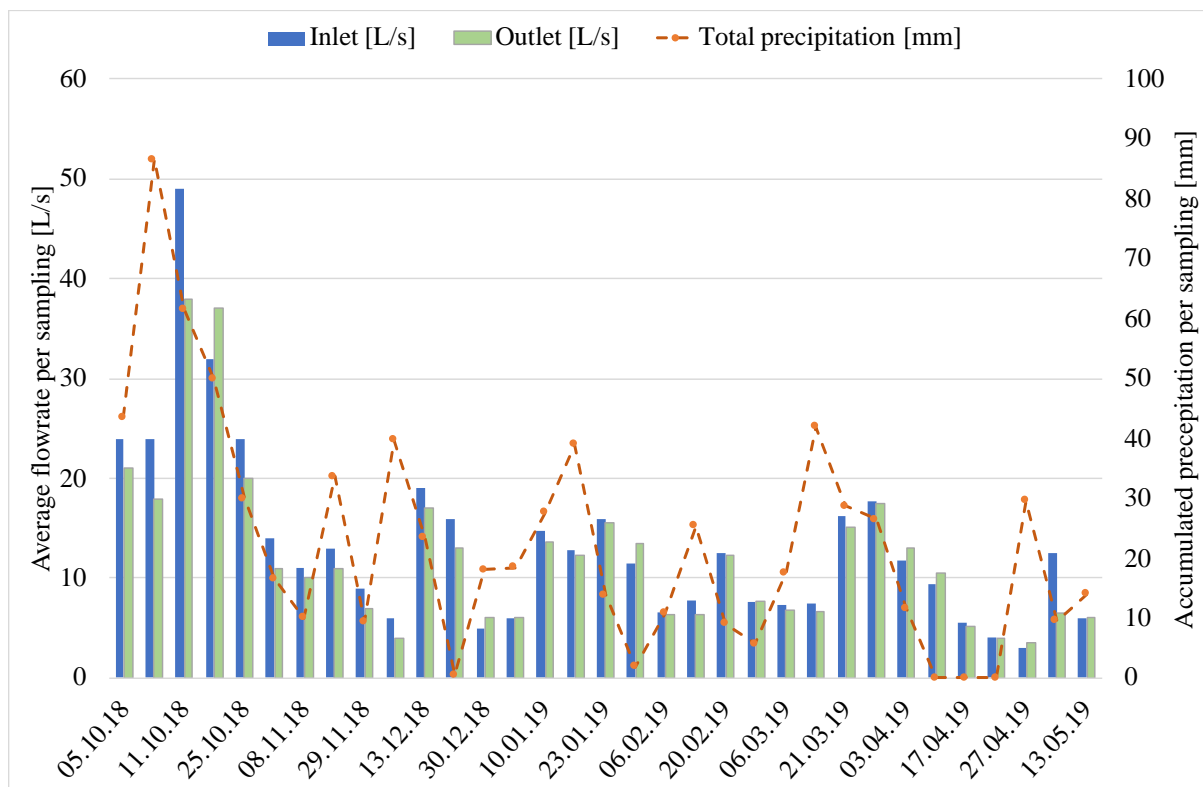


Figure 4-1 Average flowrate per sampling combined with accumulated precipitation provided by Våland mÅlestasjon (Meteorologisk institutt, 2007-2019).

The instantaneous values measured every 15 minutes by the flowmeter is presented in Figure 4-2.

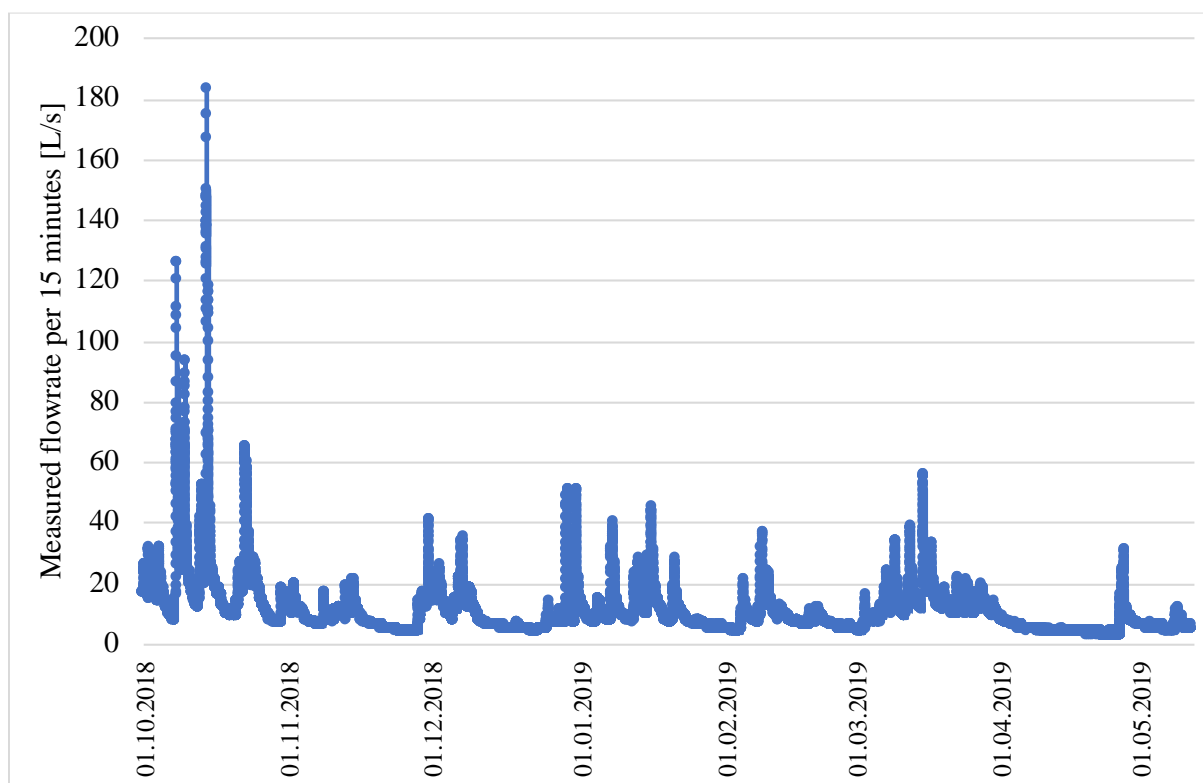


Figure 4-2 Instantaneous values measured every 15 minutes outlet flowmeter in the period 01.10.2018-13.05.2019.

4.1.2 Variations and retention of nitrogen compounds

Inlet samples were analyzed for NO_3^- and NH_4^+ from 13th of December 2018, while TN and sTN were analyzed from 30th of December 2018 and 30th of January 2019. The relative methodological standard deviations for NO_3^- , NH_4^+ and TN measurements was estimated to 1.3%, 4.3% and 8.3%, respectively (Table 4). Error bars presented in following figures are based on these values.

Two relatively large peaks were observed 30th of January and 6th of March for all parameters (Figure 4-3). It was evident that sTN constituted a large fraction of TN, and in some weeks did nitrate constitute the entire concentration. TN concentrations ranged from 4.1 mg/L to 14.4 mg/L, while sTN range from 3.1 mg/L to 14.4 mg/L. NO_3^- -concentrations seemed to follow the same pattern as TN except from having slightly less variations, ranging from 3.3 mg/L to 13.2 mg/L. NH_4^+ concentrations were relatively low throughout the period until 10th of April 2019, where it is stable at zero out the sampling period.

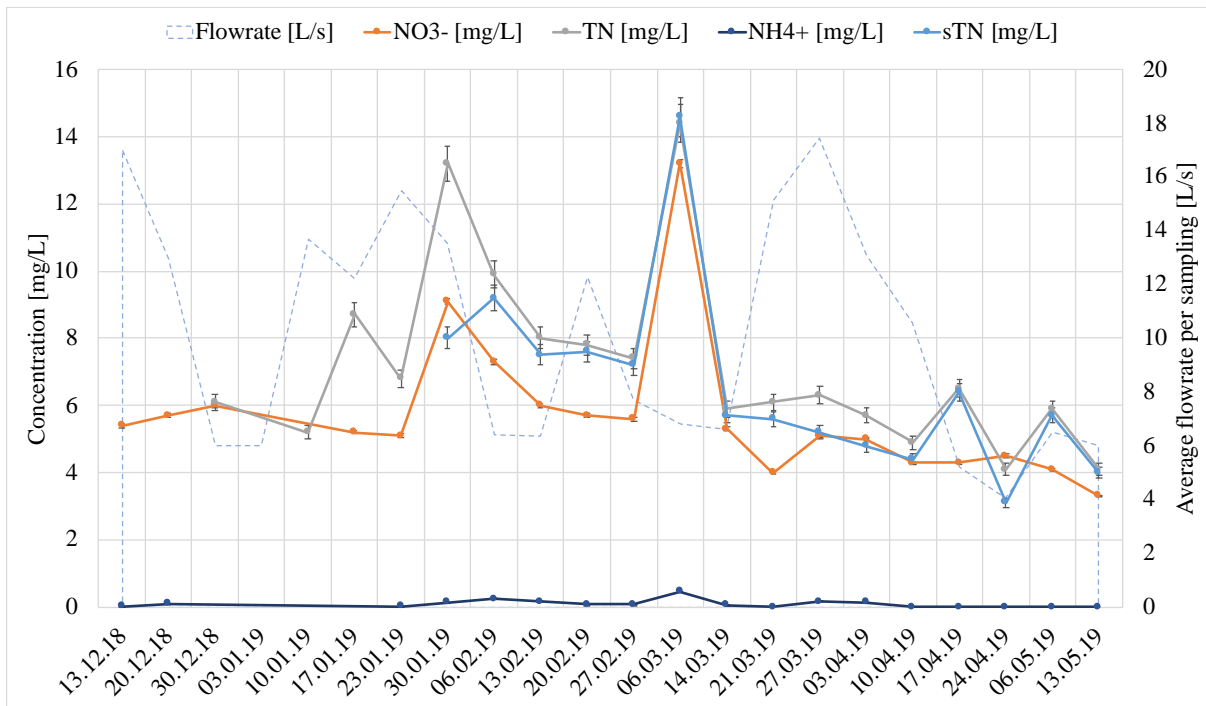


Figure 4-3 The variation of NO_3^- , NH_4^+ , TN, sTN concentrations measured at inlet of Pond 1 during weekly sampling.

Samples from the mid-pond sampler (Figure 4-4) were analyzed in the period 5th of October-15th of November and 10th of April to 13th of May. Due to sampler malfunctioning and therefore lack of data, it was difficult compare the results with the other measurement stations. However, concentrations in April was up to 3.7 mg NO₃⁻/L, 3.4 mg TN/L and 3.3 mg sTN/L higher compared to inlet samples in the same period.

Outlet samples (Figure 4-5) had a similar pattern to inlet and mid-pond samples in the beginning and end of sampling period. The concentrations are corresponding to flow pattern without any distinct peaks. In the period 1st of November 2018 until 10th of April did outlet concentrations have frequently small fluctuations compared to inlet concentrations. TN seemed to be more directly affected by the flow, while nitrate did not have the high fluctuations in periods where TN did. Notice the lower concentrations in the first high flow peak. Mass fluxes and the variations in inlet, mid-pond and outlet concentrations for the individual parameters are presented in Appendix E and D, respectively.

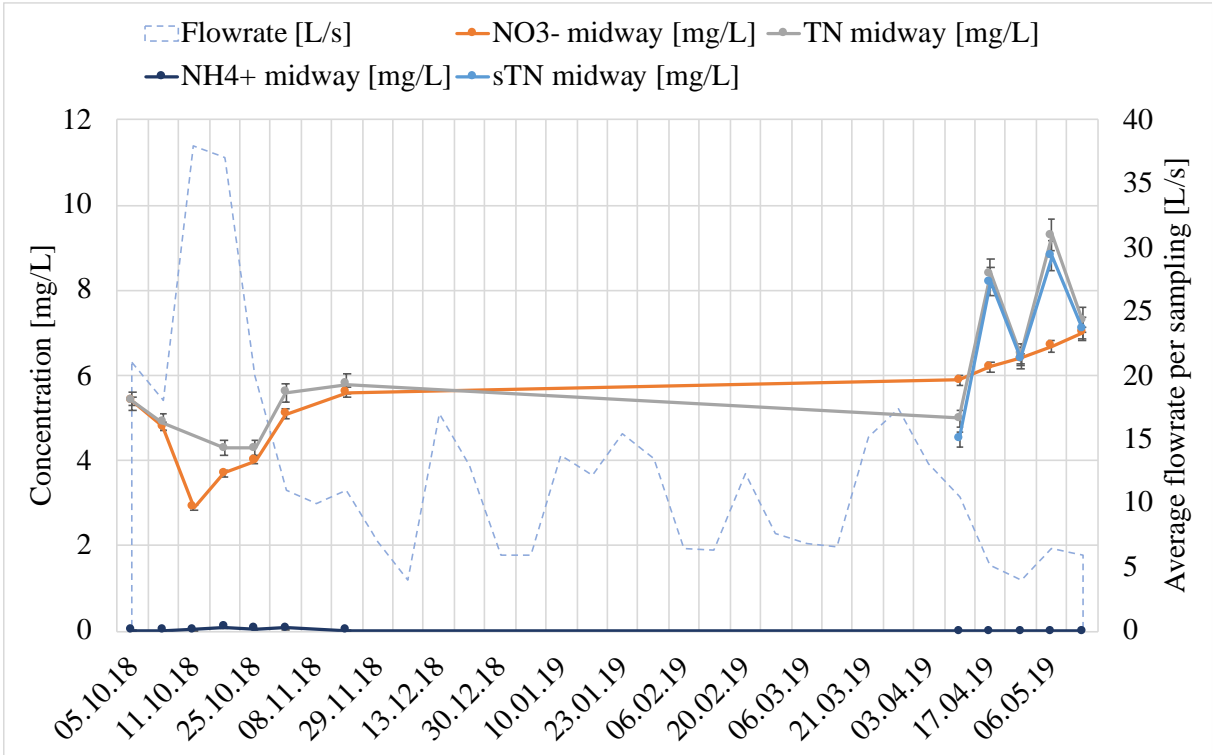


Figure 4-4 The variation of NO₃⁻, NH₄⁺, TN, sTN concentrations measured at inlet of Pond 2 (mid-pond) during weekly sampling.

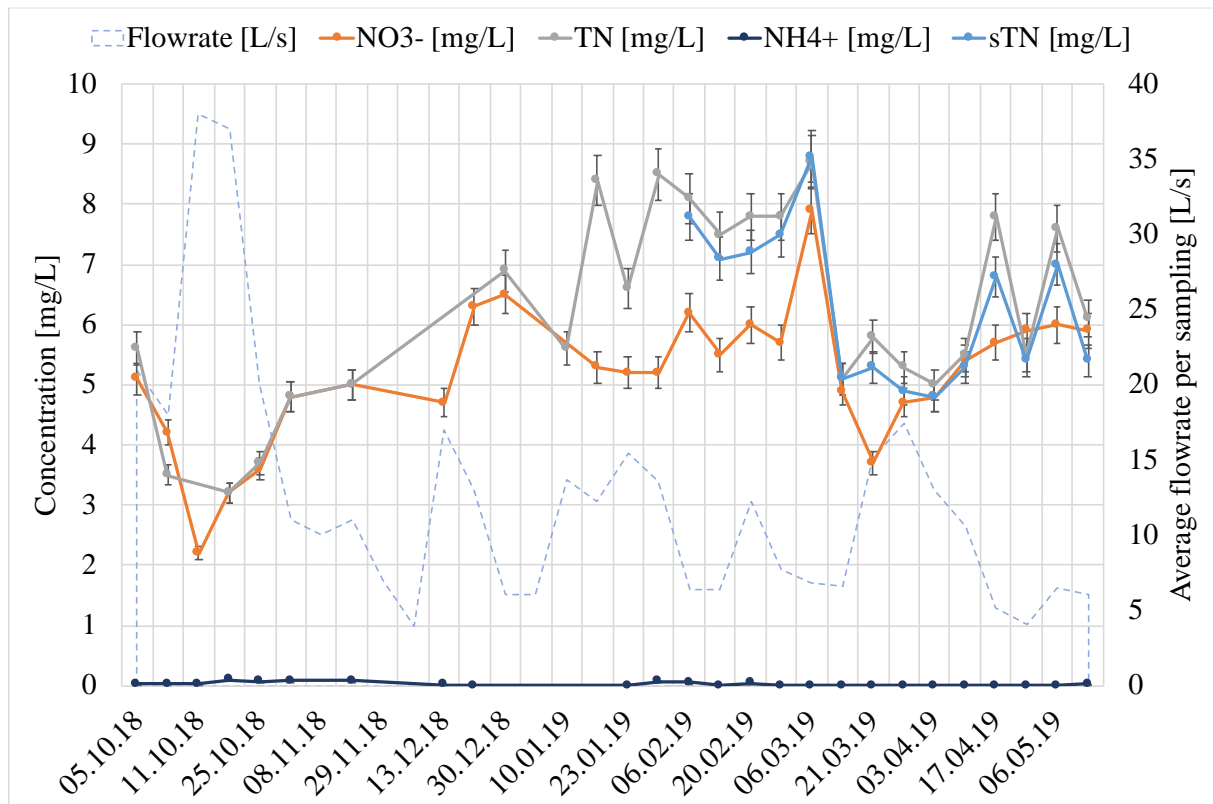


Figure 4-5 The variation of NO_3^- , NH_4^+ , TN, sTN concentrations measured at outlet of Pond 2 during weekly sampling.

The retention of nitrogen compounds and TSS was calculated by subtracting outlet from inlet mass fluxes (Table 3). The mass flux was obtained by multiplying concentrations with the hydraulic loading. The total retention of both ponds is presented in Figure 4-6, and not separately, due to lack of data from the midterm sampler. The retention efficiency was calculated by dividing the mass of nitrogen retained (kg) divided by the incoming mass in the specific period.

A positive retention represents accumulation, while a negative retention indicate that outlet concentrations are marginally higher than inlet concentrations. Two points was distinct at 38.5 kg TN/week the 30th of January and 23.5 kg TN/week the 6th of March. A negative retention was observed in April and May.

The Teledyne ISCO Signature Flow meter is by the manufacturer reported to have a standard error of 0.01-0.02% of measured flowrate (RS Hydro, 2019). The standard deviations for NO_3^- , NH_4^+ and TN retention was calculated by error propagation by multiplication from the combination of the percentile standard error of the flow meter and estimated standard deviation

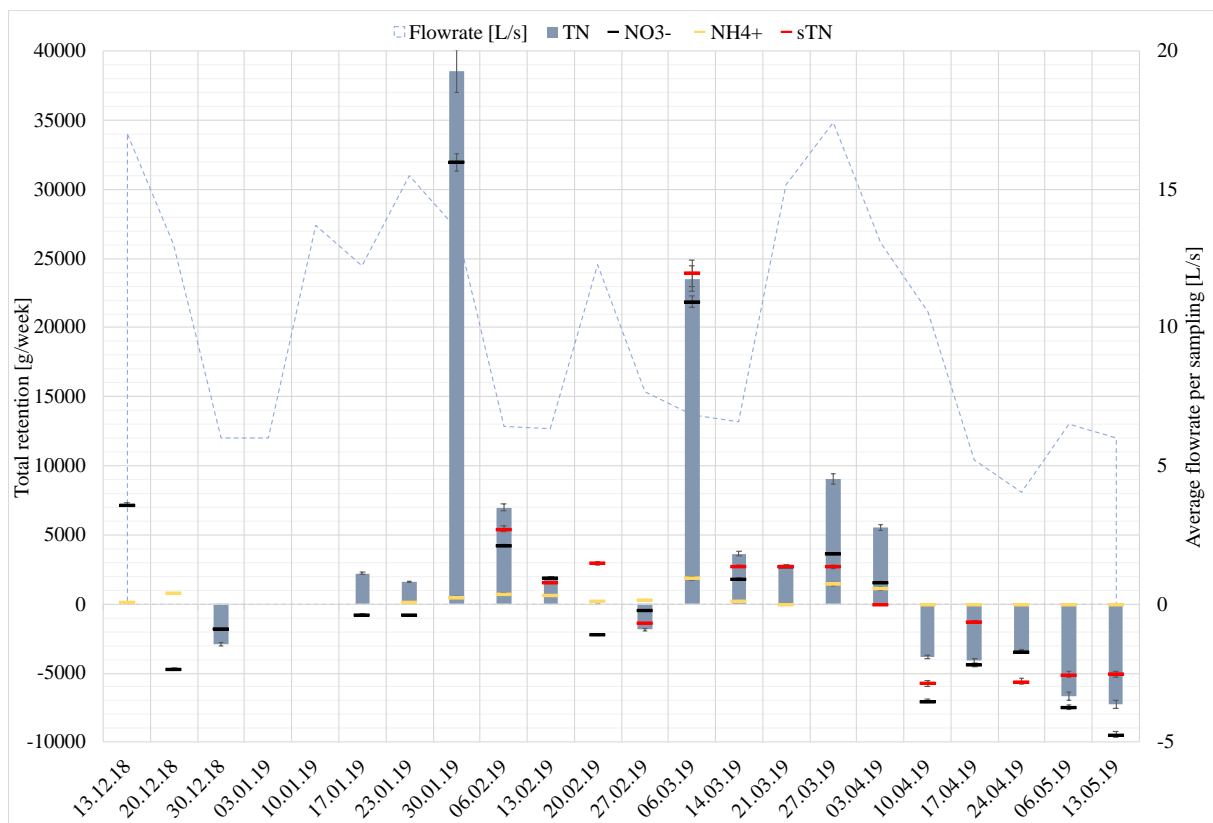


Figure 4-6 Total retention of NO_3^- , NH_4^+ and TN in Leikvollbekken during weekly sampling.

from nitrogen concentrations (Table 4). The percentile standard deviation of NO_3^- , NH_4^+ and TN retention was estimated to 2.4%, 8.5%, and 4.7%, respectively (Figure 4-6).

4.1.3 Variations in additional parameters

TSS and FSS in inlet samples were in periods remarkably higher than mid-pond and outlet samples (Figure 4-7). The parameters were measured from 11th of October and 20th of February, respectively. A high peak for TSS is observed at 35 mg/L 13th of December and 56.1 mg/L 17th of April. Inlet samples have large variations in concentration, while outlet samples are characterized by relative stable values.

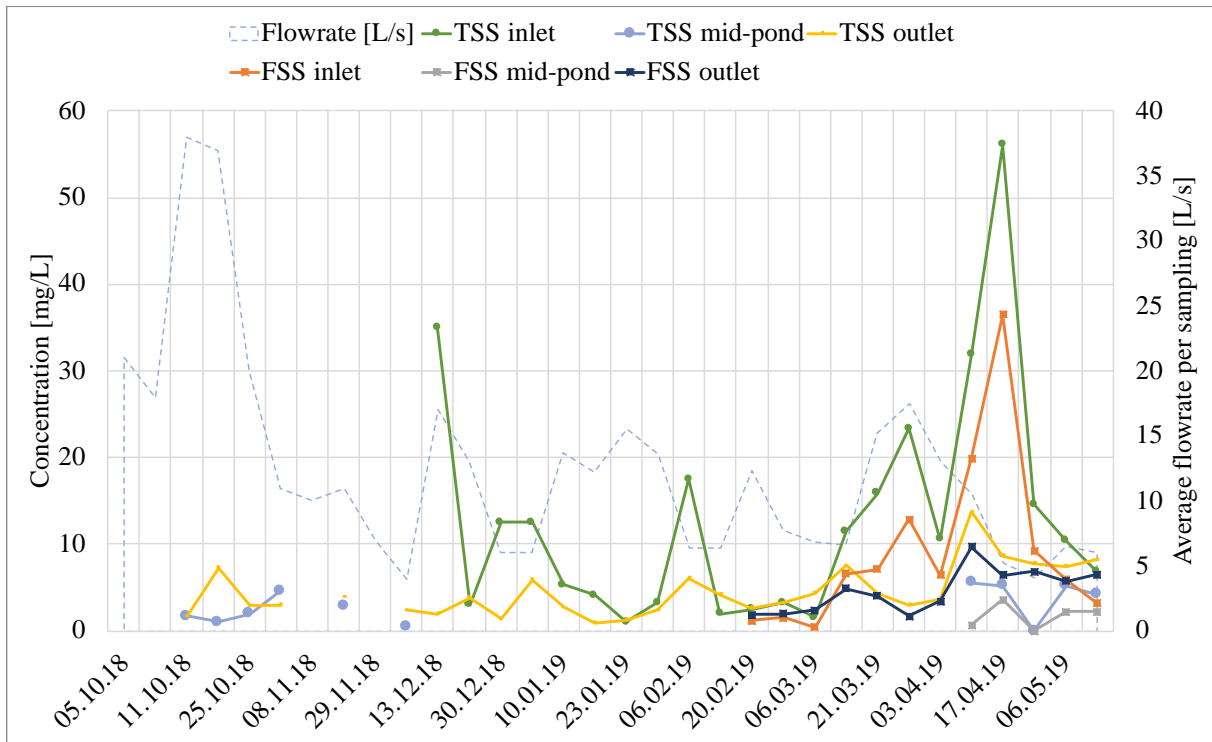


Figure 4-7 The variation in TSS and FSS concentrations in weekly water samples.

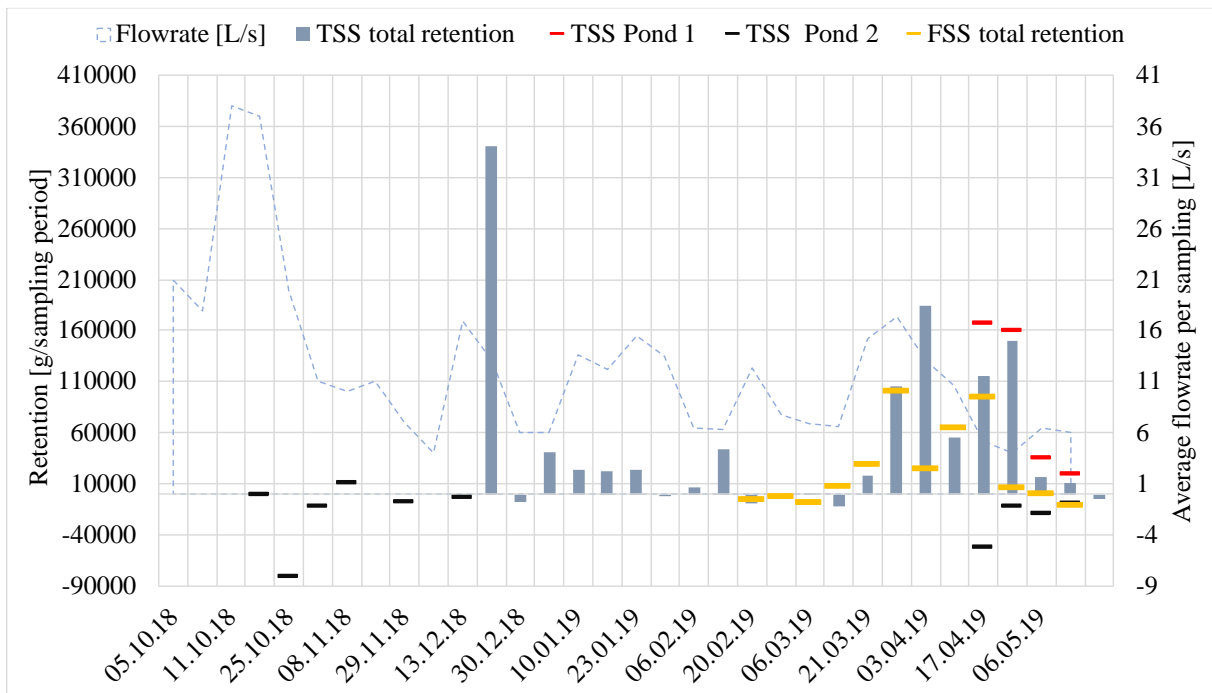


Figure 4-8 TSS and FSS retention during weekly sampling.

An overall positive retention was observed for TSS and FSS in Leikvollbekken throughout the sampling period (Figure 4-8). Pond 2 had a negative TSS retention, except for two samples. In contrast did Pond 1 have positive retention in all samples. A distinct peak was observed 20th of December 2019. Retention was not calculated for Pond 1 and 2 separately in this period due to the lack of data from mid-pond samples. Detailed data of TSS retention is presented in Table 3.

The pH values in inlet and outlet water samples alternated being highest (Figure 4-9). Inlet alkalinity and conductivity tended to be more affected of higher flowrate compared to mid-pond and outlet (Figure 4-9). In general, if excluding the peak in the period 30th of January to 6th of February was outlet alkalinity highest. Color in samples varied with flow, with highest value measured to 68.1 mg Pt/L in an outlet sample (Figure 4-10).

Table 3 Total retention and retention efficiency of NO₃⁻, NH₄⁺, TN, sTN and TSS and FSS in weekly water samples.

	Retention [kg/sampling period*]	Retention [g/(m²*sampling period*)]	Retention efficiency [%]
NO₃⁻	33.8	24.7	6.1
NH₄⁺	7.2	5.3	87.1
TN	68.6	50.2	9.4
sTN	17.9	13.1	3.8
TSS	1121.2	820.6**	67.0
FSS	299.0	218.9**	51.6

* The sampling period is unique for each parameter.

** TSS and FSS is shown in kg instead of g.

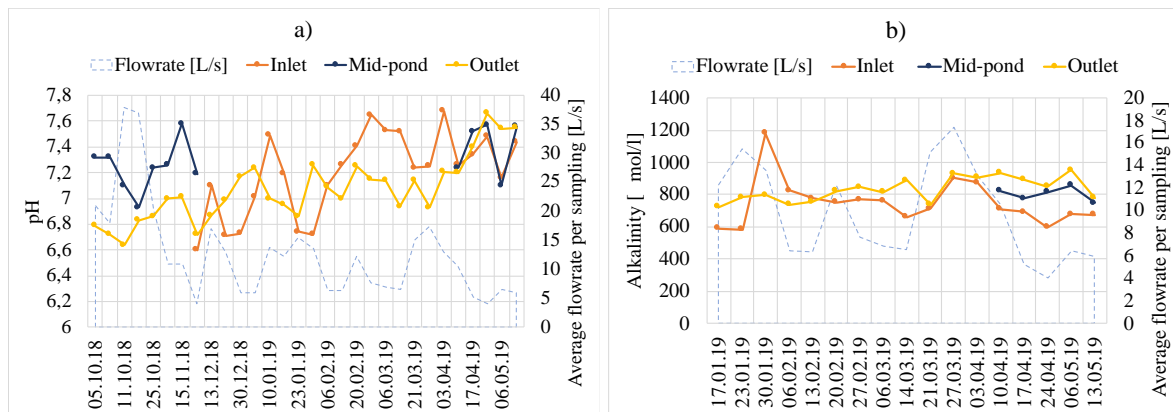


Figure 4-9 Variations in a) pH and b) alkalinity in weekly water samples (05.10.2018-13.05.2019)

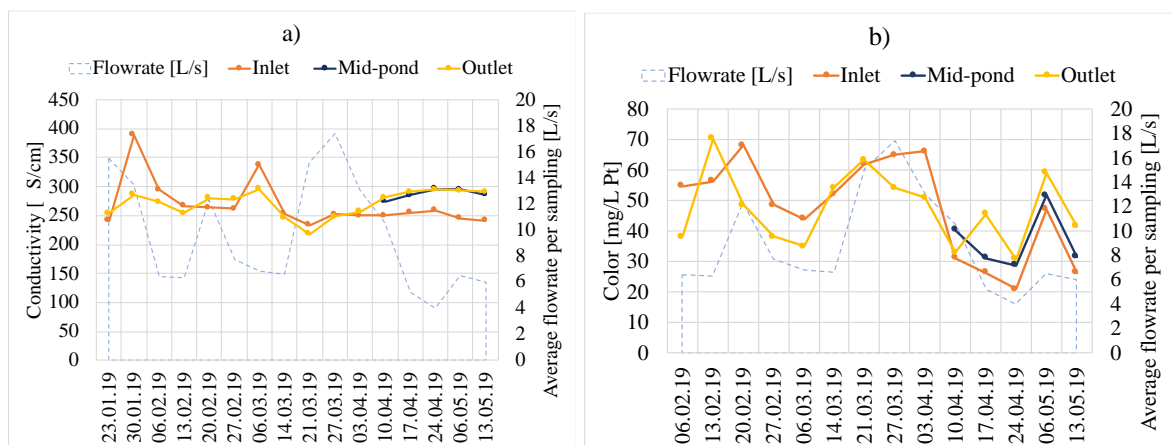


Figure 4-10 Variations in a) conductivity and b) color in weekly water samples (05.10.2018-13.05.2019)

4.1.4 Error- and statistical analysis

The mean standard deviation of Spectroquant Cell Test was based on three parallels in inlet and three parallels in outlet water samples, collected every week in the period 5th of October to 13th of December 2018. Standard deviation of ISE was calculated from two parallels, including the standard solutions used for calibration curves. Parallels were not taken for ISE + AgSO₄ and The Standard Addition method, nor The Zinc Reduction method. Error bars in graphs describing nitrogen compounds are based on these values.

Table 4 Mean standard deviation presented in concentration and percentage estimated for NO_3^- , NH_4^+ and TN.

Test	Parameter	Standard deviation [mg/]	Standard deviation [%]	n
Spectroquant Cell Test	NO_3^-	0.2	1.3	48
	NH_4^+	0.004	8.3	48
	TN	0.2	4.3	42
ISE	NO_3^-	0.2	6.7	34

Regression analysis was performed on combinations of parameters used in analyzing weekly samples (Table 5). Additional combinations and significant correlations in Table 5 are presented in Appendix G. Mass fluxes have not been included as they are based on the same flow.

Table 5 Regression analysis performed on parameters in weekly water samples.

Parameters	Coefficient	R^2	p-value	n
TN [kg/week] vs. Flow [L/s]	0.90	0.11	0.217	16
Particulate TN [kg/week] vs. Flow [L/s]	0.34	0.25	0.067	14
NH_4^+ [g/week] vs. TN [kg/week]	28.10	0.34	0.019	16
NO_3^- [kg/week] vs. TN [kg/week]	0.88	0.97	<0.001	17
Particulate TN [kg/week] vs. TSS [kg/week]	0.02	0.17	0.138	14
TN [mg/L] vs. Alkalinity [$\mu\text{mol/L}$]	0.01	0.01	0.679	28
TN [mg/L] vs. Conductivity [$\mu\text{S/cm}$]	0.06	0.53	<0.001	28
TN [mg/L] vs. Color [mg Pt/L]	0.03	0.03	0.386	28

4.2 Storm event

The storm event lasted 24 hours from 26th to 27th of April. Inlet, mid-pond and outlet samplers collected hourly samples starting at 18:00 the 26th. Due to expected rain the 24 hours before the storm event was 2x12hour composite samples taken for inlet, mid-pond and outlet. During the storm event did the samplers sample a volume of 200 ml each 15 minutes, 800 ml in each hourly sampling bottle. All 77 samples were analyzed for NO₃⁻, NH₄⁺, TN, TSS, pH, conductivity, alkalinity and color.

4.2.1 Hydraulic load

The flowrate for the inlet and outlet of pond 2 were measured every 15 minutes, increasing from 2 L/s to approximately 30 L/s (Figure 4-11). Prior the storm event a dry period of 23 days resulted in low stable flowrate in both measuring locations.

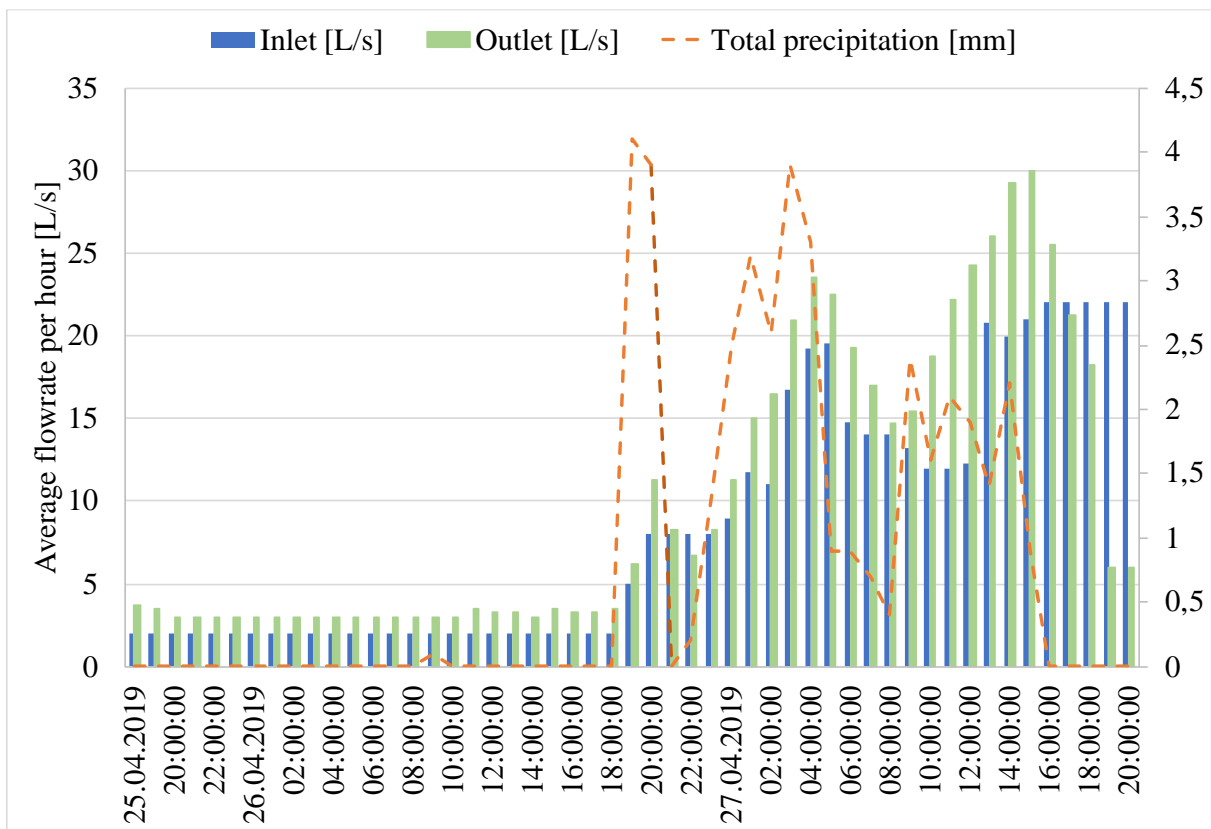


Figure 4-11 Average flowrate per hour combined with accumulated precipitation per hour provided by Våland målestasjon (Meteorologisk institutt, 2007-2019).

Outlet flowrate was slightly higher than inlet flowrate in the period before and during the storm event. The reason is better quality of the probe that measured outlet flow. Three distinct peaks were observed at 9.6 L/s, 21.4 L/s and 25.5 L/s. The peaks coincided with the accumulated precipitation provided by yr.no (Figure 3-7). At 17:00 the outlet rate rapid decreased and inlet flowrate was stable at maximum flow of 22 L/s.

4.2.2 Variations and retention of nitrogen compounds

NO₃⁻ concentrations during storm event were measured using ISE added silver sulfate. Samples measured with ISE showed higher values compared to Spectroquant Cell Test. The NO₃⁻-values used in this section were therefore adjusted by Equation 9 (4.3.3 Statistical analysis of nitrate methods).

Equation 9 Approach of concentration by Spectroquant Cell Test by ISE and conductivity

$$y = 0.64 * ISE \left[\frac{mg}{L} \right] + 0.01 * Conductivity \left[\frac{\mu S}{cm} \right] - 2.1$$

The flowrate plotted against parameters in this section are based on flowrate measured at the outlet of the constructed wetland (3.3.4 Flow measurements). The percentile standard deviations presented as error bars in following figures are based on values in Table 4, and do not include the error introduced by the recalculation (Appendix H).

Samples were taken at the same time every hour for 24 hours, except mid-pond sampler took 23. It is clear that nitrate represented a large fraction of total nitrogen also during storm event (Figure 4-12). NO₃⁻ and TN showed a trend of following the flow pattern while NH₄⁺ slightly increased as higher flow occurred. However, NO₃⁻ and NH₄⁺ was relatively stable compared to TN which was as high as up to 13 mg/L after the first flow peak.

Similarly, as for inlet samples did also the concentrations in mid-pond samples follow the flow pattern (Figure 4-13). However, the concentrations for NO₃⁻ and TN were higher compared to inlet in several samples. In addition, TN was more stable over time.

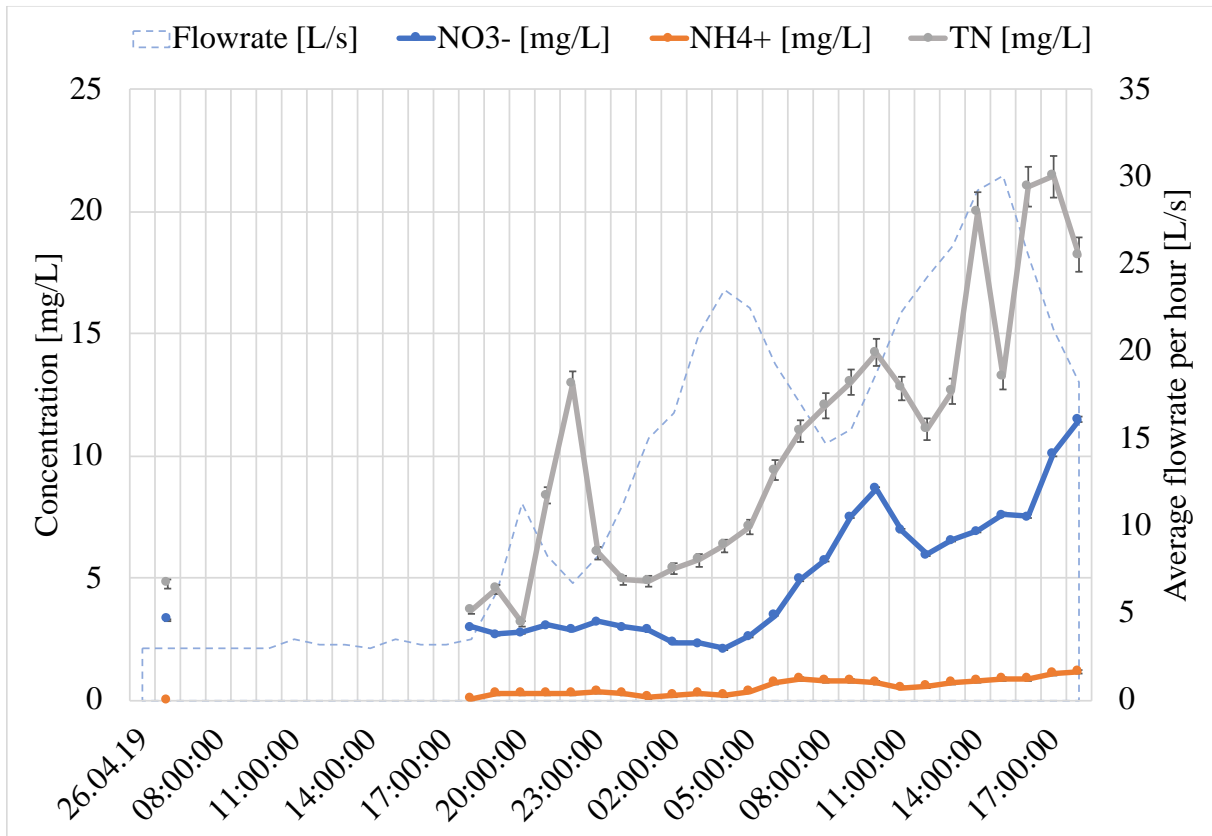


Figure 4-12 The variation of NO_3^- , NH_4^+ and TN concentrations measured at inlet of Pond 1 during storm event..

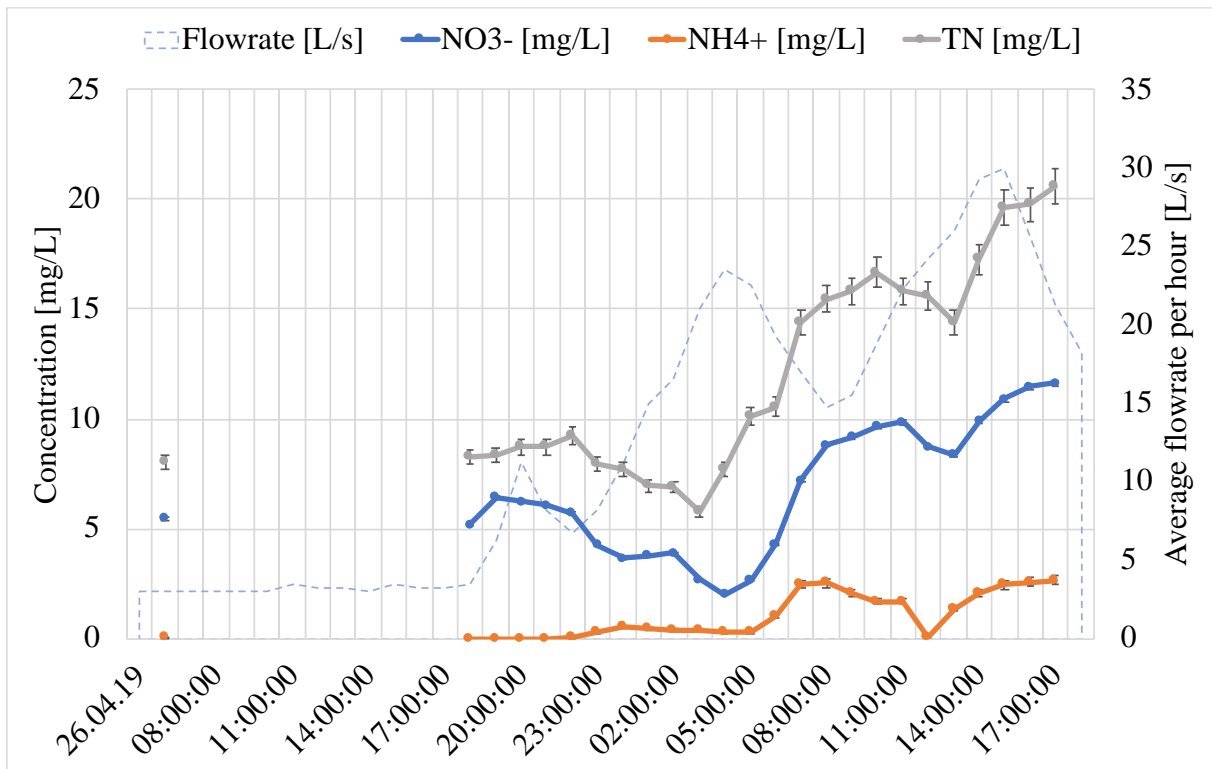


Figure 4-13 The variation of NO_3^- , NH_4^+ and TN concentrations measured at inlet of Pond 2 (mid-pond) during storm event..

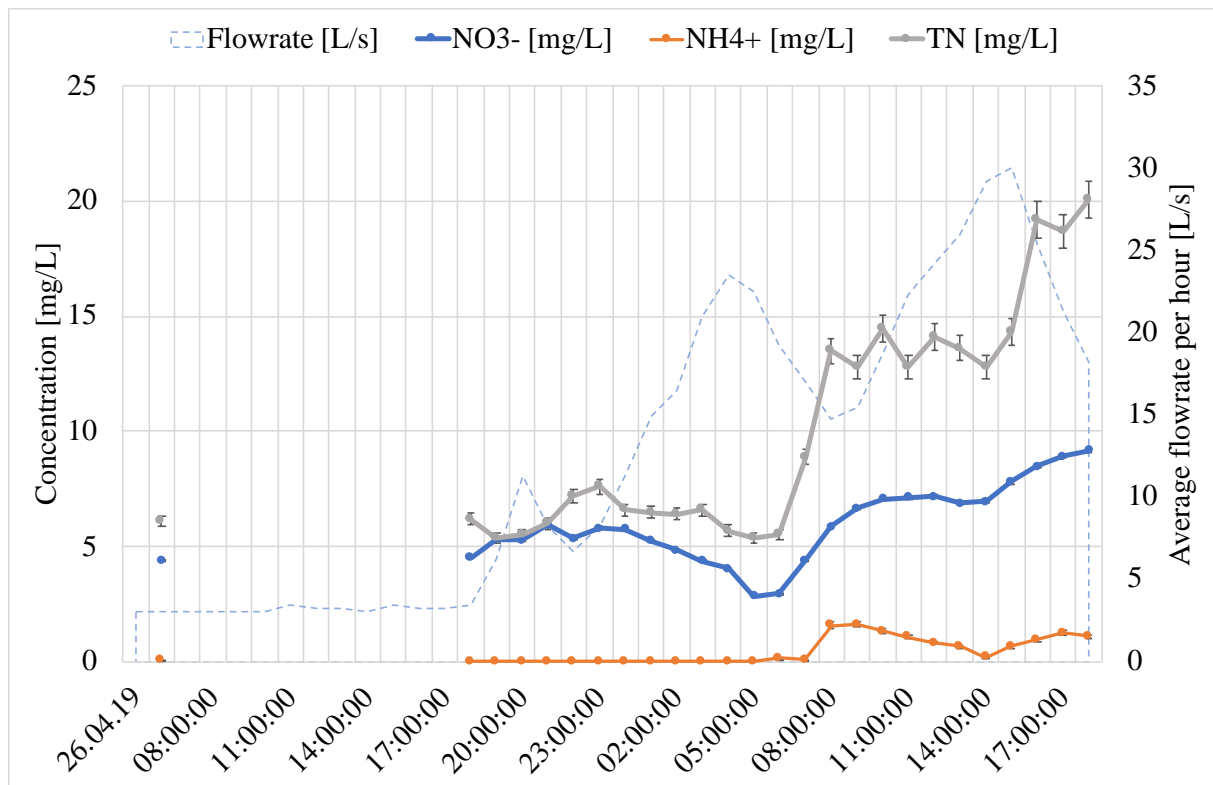


Figure 4-14 The variation of NO_3^- , NH_4^+ and TN concentrations measured at outlet of Pond 2 during storm event..

The concentration of NH_4^+ was measured below the detection limit until 21:00 the 26th of April. A steeper increase in NH_4^+ was observed in the second flow peak, followed by a decrease as the flow rate became lower. The same pattern was shown for all three parameters approximately from 03:00 27th of April until the sampling was over.

The shape of the concentration curves was not as defined for outlet as for inlet and mid-pond (Figure 4-14). NH_4^+ was not observed until 02:00 the 27th of April except from very low concentration in the composite samples from the first 12 hours the day before.

Nitrogen retention was calculated for Pond 1, Pond 2 and in total. Pond 1 had an overall negative retention for NO_3^- , NH_4^+ and TN (Figure 4-15) increasing in parallel with flowrate. NO_3^- tended to reflect the first and third flow peak. No large variations in NH_4^+ -retention was observed until 06:00 27th of April. TN had an increasing negative retention pattern with a distinct positive retention prior to third flow peak, measured to 287.8 g/hour.

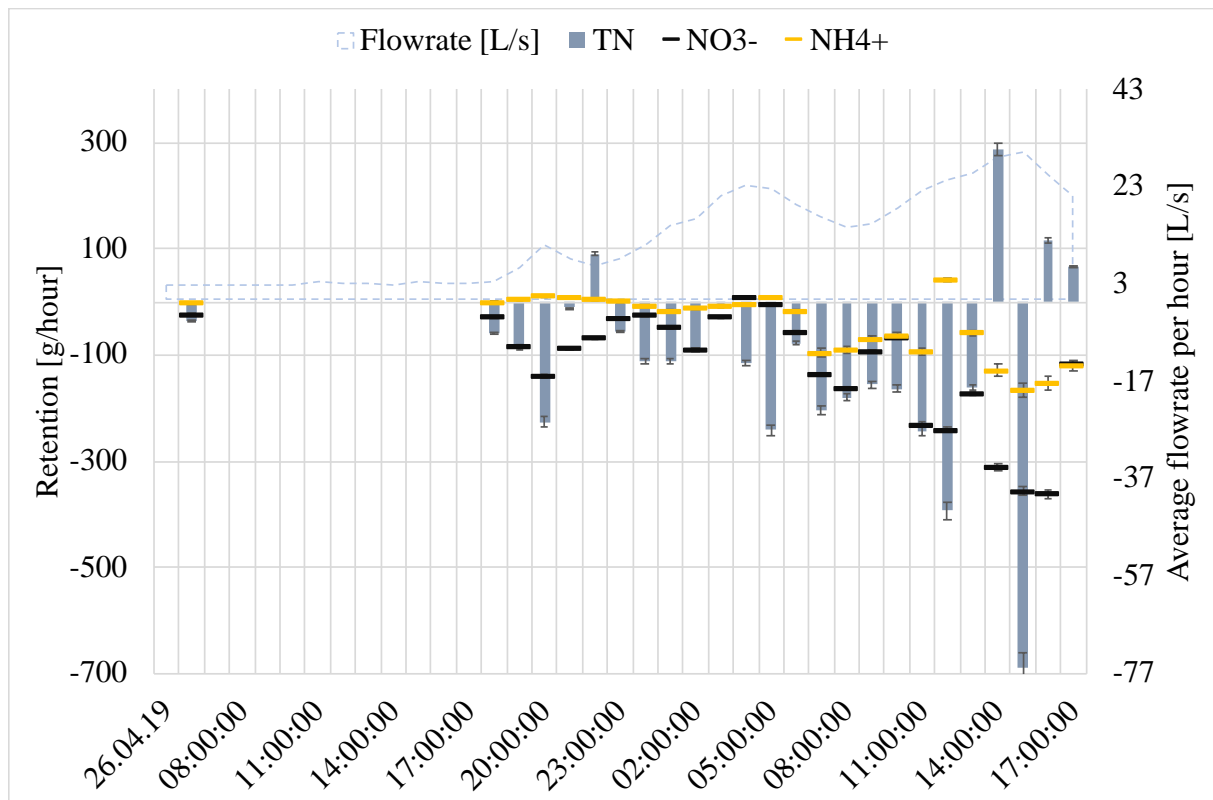


Figure 4-15 The hourly retention of NO_3^- , NH_4^+ and TN in Pond 1 during storm event.

Pond 2, in contrast to Pond 1, had an overall positive retention (Figure 4-16). NO_3^- varied from being negative after first flow peak, to have a remarkably increasing retention during flow peak two and three. NH_4^+ and TN concentrations followed the same pattern as all three peaks.

The total retention (Figure 4-17) varied throughout the storm event. NO_3^- had an increasing negative retention during first and second flow peak, and a retention that alternated with being positive and negative after second flow peak. The NH_4^+ retention was opposite, having positive retention before alternating. The retention in Pond 1, Pond 2 and in total had in common the distinct positive retention of TN 14:00 the 27th of April.

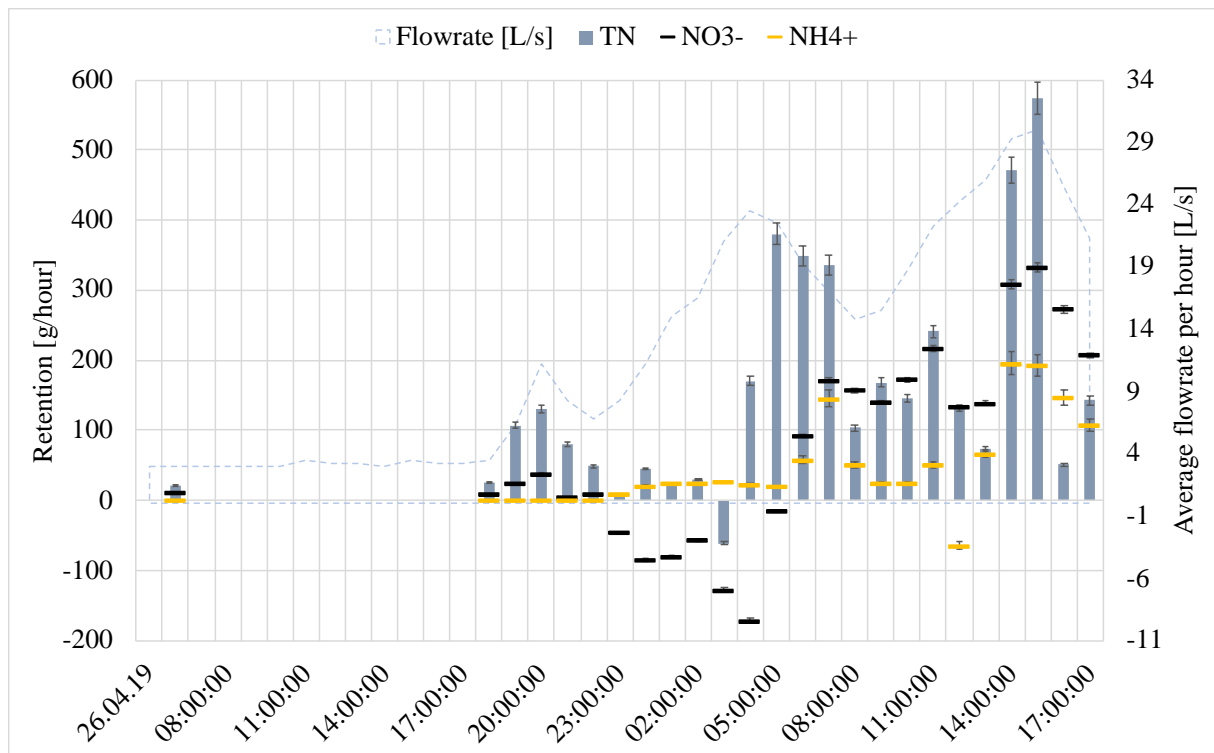


Figure 4-16 The hourly retention of NO_3^- , NH_4^+ and TN in Pond 2 during storm event.

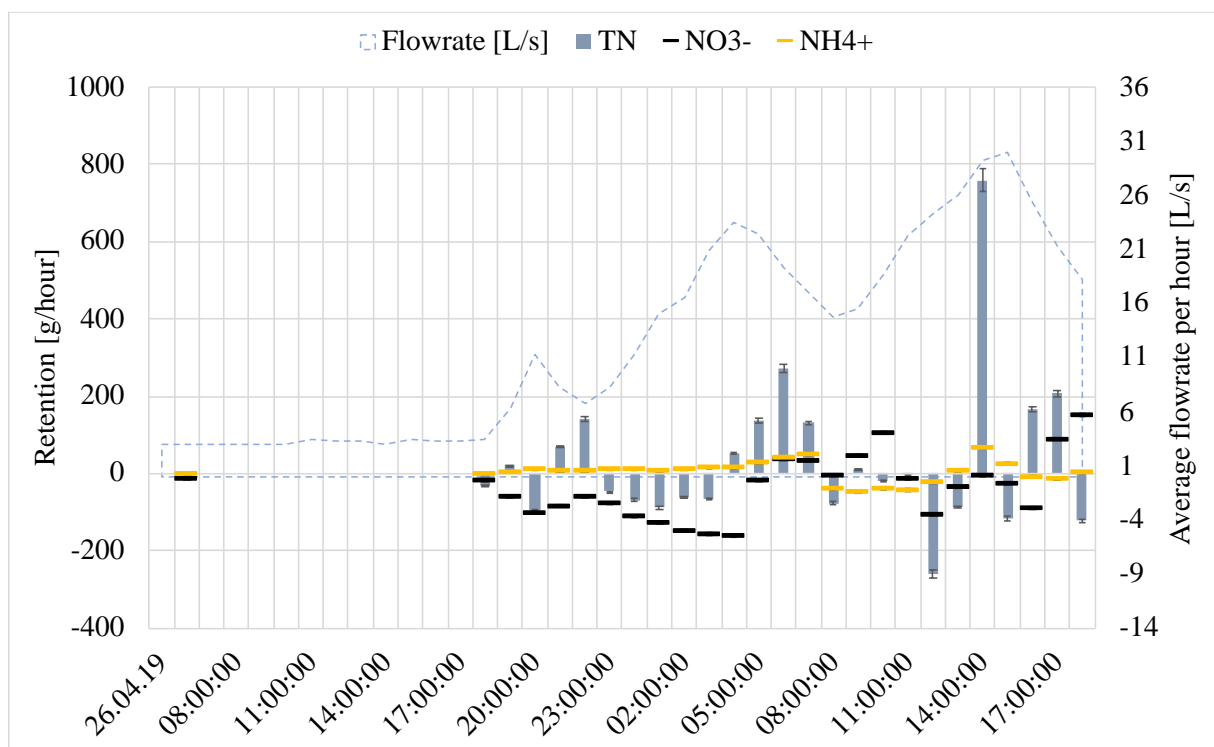


Figure 4-17 The hourly retention of NO_3^- , NH_4^+ and TN in Leikvollbekken during storm event.

4.2.3 Variations in additional parameters

TSS concentrations were relatively stable the 24 hours prior to the storm event with highest concentration of approximately 3.0 mg/L out of the wetland, followed by the mid-pond and inlet concentration of 0-1.6 mg/L (Figure 4-18). TSS inlet increased rapidly after the first flow peak up to 106.3 mg/L before approaching its initial value. The first peak had a concentration about 250 % higher than second highest. Three smaller peaks at 35.8 mg/L, 36.7 mg/L and 33.9 mg/L were observed after.

TSS outlet followed the same trends as TSS inlet but delayed. First peak at 42.6 mg/L was detected one hour later than inlet concentration peak. The third peak was detected at the end of storm event with a concentration of 28.7 mg/L, close to five hours after the third peak for TSS inlet. TSS mid-pond was more stable over time, slightly following the flow pattern.

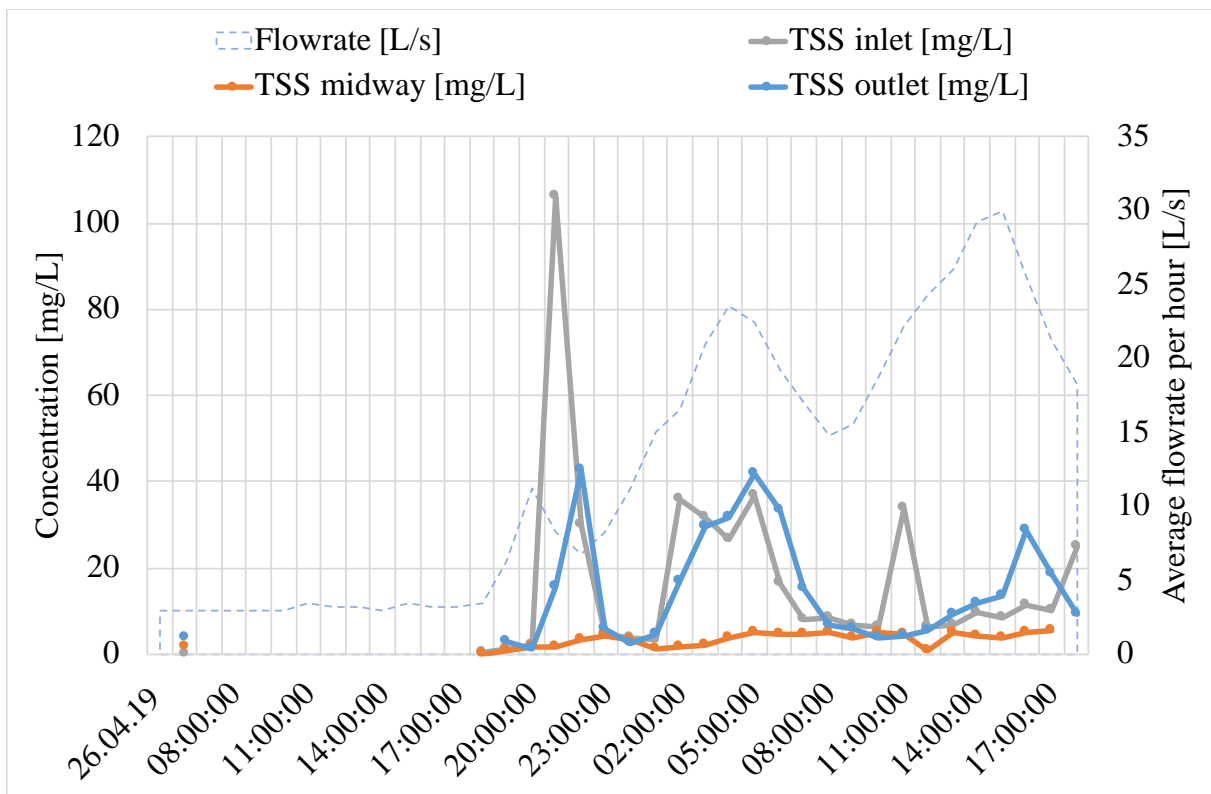


Figure 4-18 TSS concentration in inlet, mid-pond and outlet water samples during storm event.

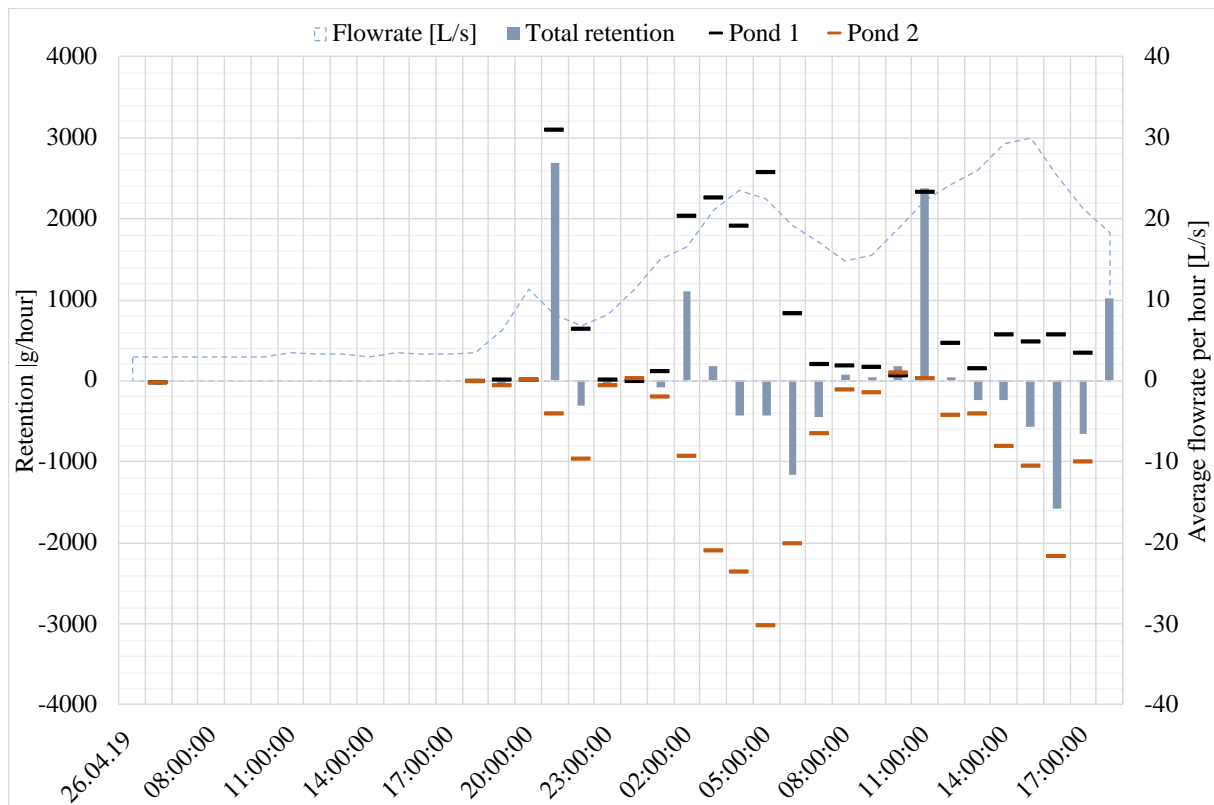


Figure 4-19 TSS retention in Pond 1, Pond 2 and Leikvollbekken in total during storm event.

The overall TSS retention in Leikvollbekken during storm event was characterized by positive retention prior to flow peaks and negative retention during the flow peaks (Figure 4-19). The retention for Pond 1 and Pond 2 was inverted, showing a positive and negative retention, respectively (Table 6).

Table 6 Retention of parameters in Pond 1, Pond 2 and Leikvollbekken in total during storm event.

Area	Parameter	Retention [kg/sampling period]	Retention [g/(m ² *sampling period)]	Retention efficiency [%]
Pond 1	NO ₃ ⁻	-2.2	-3.0	-0.2
	NH ₄ ⁺	-0.9	-1.3	-95.9
	TN	-1.7	-2.3	-8.9
	TSS	20.8	28.3	78.6
Pond 2	NO ₃ ⁻	1.3	2.0	11.4
	NH ₄ ⁺	1.1	1.7	55.6
	TN	2.5	3.9	12.3
	TSS	-19.2	-30.6	-339.1
Total	NO ₃ ⁻	-0.9	-0.7	-10.7
	NH ₄ ⁺	0.1	0.1	13.1
	TN	0.8	0.6	4.5
	TSS	1.6	1.2	6.0

Decreasing values of pH, alkalinity (Figure 4-20) and conductivity (Figure 4-21) were observed during the storm event. The pH values in inlet, mid-pond and outlet measuring locations did all show the same trend. However, pH-values measured at inlet was in average 0.28 lower compared to the pH-values in mid-pond and outlet samples.

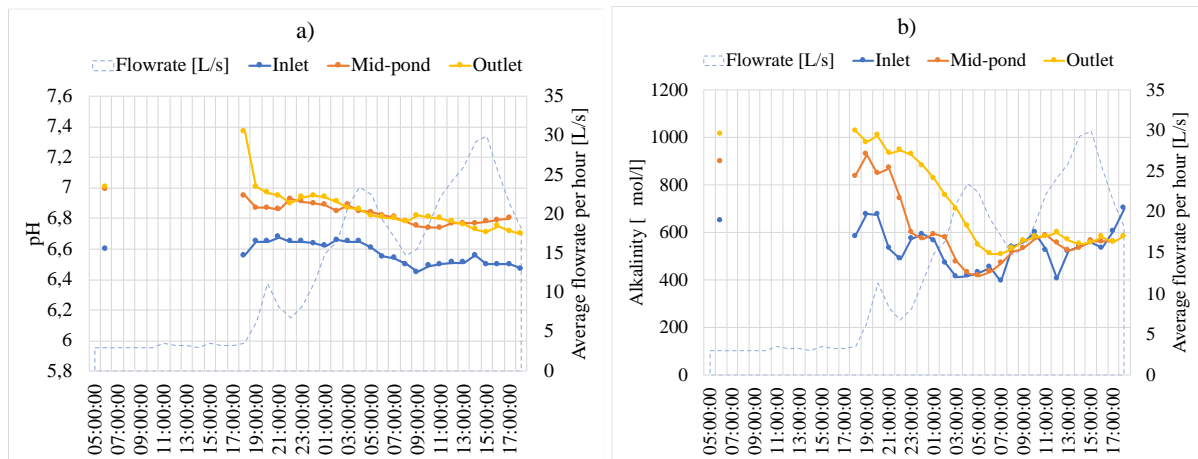


Figure 4-20 Variations in a) pH and b) alkalinity during storm event (26.04.2019-27.04.2019)

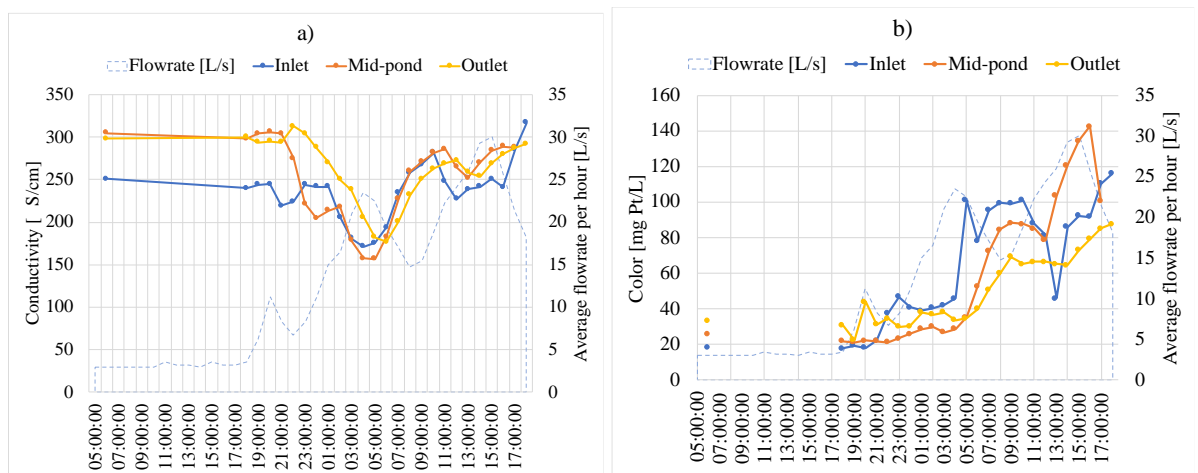


Figure 4-21 Variation in a) conductivity and b) color during storm event (26.04.2019-27.04.2019)

The color in the water samples increased further into the storm event (Figure 4-21). Inlet and mid-pond samples were more affected by the flow, while outlet increased steadily over time. Outlet samples analyzed prior to the storm event had stronger color compared to mid-pond and inlet samples.

4.2.4 Statistical analysis

Regression analysis was performed on flow, nitrogen, TSS and color concentrations in storm event samples from inlet and outlet of Pond 1 and 2, respectively (Table 7). Scatterplots of significant correlations in Table 7 and a selection of additional combinations are presented in Appendix G.

Table 7 Regression analysis performed on flow, NO_3^- , NH_4^+ , TN, TSS and color.

	Parameters	Coefficient	R ²	p-value	n
Inlet Pond 1	TN [mg/L] vs. Flow [L/s]	0.42	0.31	0.004	25
	NO_3^- [mg/L] vs. TN [mg/L]	0.42	0.74	<0.001	25
	NH_4^+ [mg/L] vs. TN [mg/L]	0.05	0.73	<0.001	25
	TN [mg/L] vs. TSS [mg/L]	-0.01	0.00	0.810	25
	TN [mg/L] vs. color [mg Pt/L]	0.12	0.56	<0.001	25
Outlet Pond 2	TN [mg/L] vs. Flow [L/s]	0.36	0.29	0.005	25
	NO_3^- [mg/L] vs. TN [mg/L]	0.30	0.78	<0.001	25
	NH_4^+ [mg/L] vs. TN [mg/L]	0.09	0.68	<0.001	25
	TN [mg/L] vs. TSS [mg/L]	-0.06	0.02	0.454	25
	TN [mg/L] vs. color [mg Pt/L]	0.24	0.93	<0.001	25

4.3 Supplementary results

Supplementary results include the grab sample taken from the “oily” surface area (Figure 3-4), reference samples taken from Store Stokkavatn and Madlabekken (Figure 3-11) and a statistical analysis of nitrate methods. The grab sample was taken to investigate if the area differed from the concentrations measured in the sampling locations, or if the area could have an effect on measured values downstream. Reference samples from Store Stokkavatn and Madlabekken served two purposes; to compare values from Leikvollbekken with the lake receiving the water and to test the nitrate methods with samples expected to have lower values. A statistical analysis of nitrate methods was performed due to discrepancies between the Spectroquant Cell Test to measure nitrate concentration in weekly water samples and ISE Nitrate Electrode used on samples from storm event.

4.3.1 Grab sample from “oily” surface area

The grab sample was taken 20th of February 2019. The phenomena were also seen in other locations (Pond 1) the few weeks after first time observed. A conductivity of 520 $\mu\text{S}/\text{cm}$ and alkalinity of 3690 $\mu\text{mol}/\text{L}$, in addition to a relatively high NH_4^+ -concentration measured to >3 mg/L (Table 8). Figure 4-22 illustrate the contrast of grab sample compared to the other samples taken.

Table 8 Measured nitrogen compounds in inlet and outlet of Leikvollbekken compared to the grab sample.

Parameter	Inlet [mg/L]	Outlet [mg/L]	Grab sample [mg/L]
NO_3^-	5.7	6.0	0.6
NH_4^+	0.07	0.04	> 3.0
TN	7.8	7.8	7.4

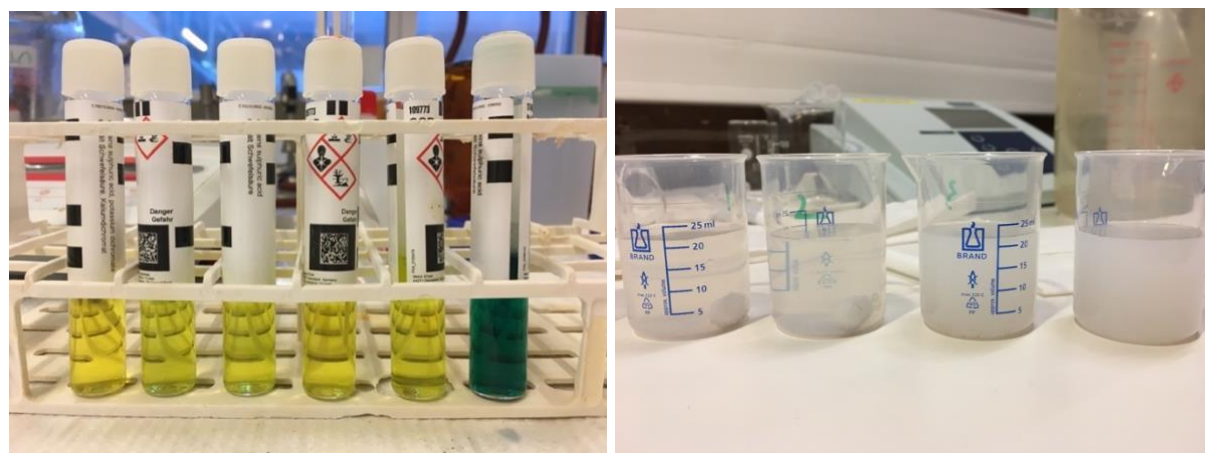


Figure 4-22 To the left: NH_4^+ analysis of blank, inlet, outlet, Store Stokkavatn, Madlabekken and the grab sample from the "oily surface" (20.02.2019). Last sample shows a distinct green color indicating high NH_4^+ content. To the right: Silver chloride precipitated due to chloride present in the water samples during ISE analysis. This was clearly observed in the period 6th - 27th of February 2019. From left to right: inlet, outlet, Store Stokkavatn and Madlabekken.

4.3.2 Reference samples

Grab samples from Store Stokkavatn and Madlabekken were taken in the period 17th of January to 17th of April 2019. Samples were analyzed for NO₃⁻, NH₄⁺, TN (Figure 4-23), pH, conductivity, alkalinity and color (Appendix K) and are plotted against the total accumulated precipitation obtained from “Våland målestasjon.

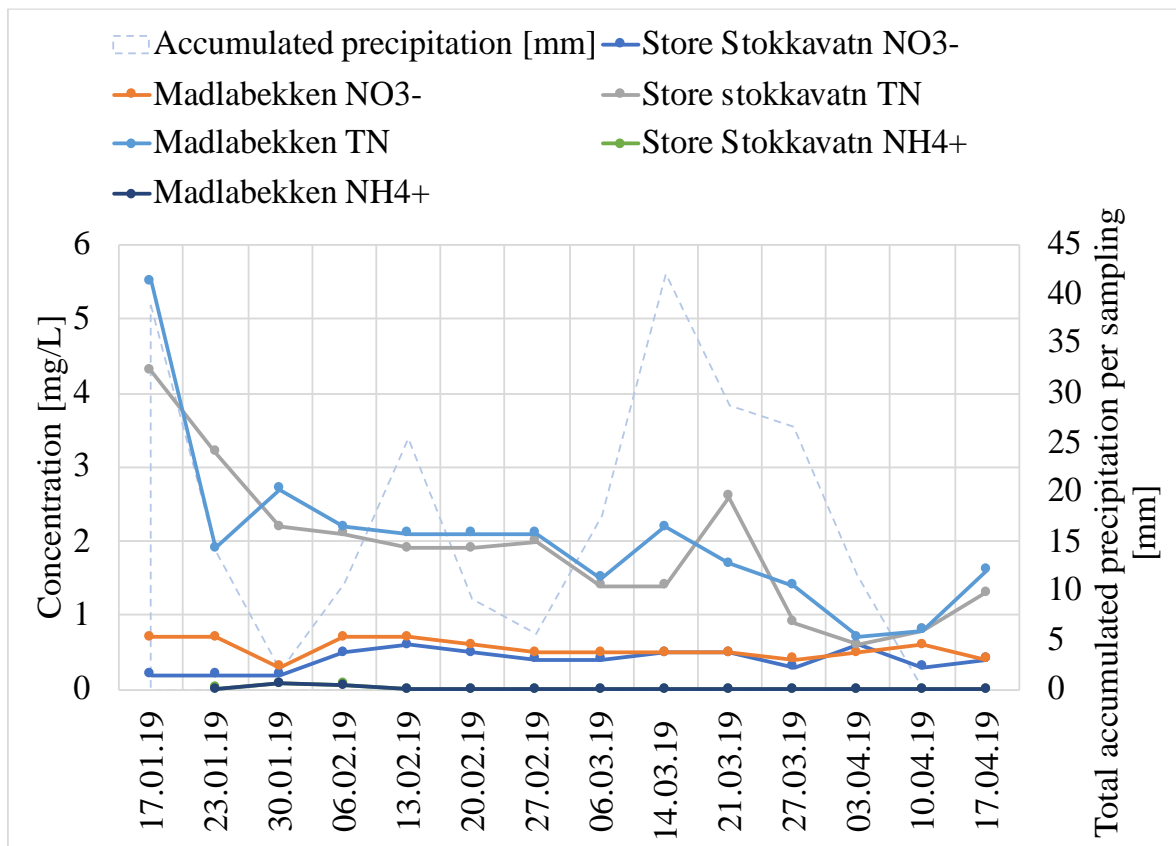


Figure 4-23 variations of NO₃⁻, NH₄⁺ and TN concentrations in samples from Store Stokkavatn and Madlabekken.

4.3.3 Statistical analysis of nitrate methods

NO₃⁻ was measured by two different methods. Spectroquant Cell Tests were used on weekly water samples and ISE Nitrate Electrode was used on samples from the storm event. During the comparison of the methods, great differences were discovered. ISE showed higher values in the samples. The hypothesis was that ions present in the water samples from Leikvollbekken interfered with the electrode.

Table 9 Results of backwards elimination of multiple regression analysis based on 52 water samples NO_3^- concentration measured by Spectroquant Cell test as the dependent variable and ISE (+silver sulfate), conductivity, pH and alkalinity as the independent

Added AgSO_4	Step	ISE	Conductivity	pH	Alk _e	r ²	r ² adjusted	F	p
NO	1	<0.001	0.002	0.044	0.045	0.989	0.989	1098.5	<0.001
YES	1	<0.001	0.001	0.087	0.307	0.984	0.984	768.8	<0.001
	2	<0.001	<0.001	0.055		0.985	0.984	1023.3	<0.001
	3	<0.001	<0.001			0.983	0.983	1448.1	<0.001

To investigate the relationship between the two methods were 52 independent weekly water samples analyzed by Spectroquant Cell Test and ISE. In addition, pH, alkalinity and conductivity were measured. Multiple regression was performed on the water samples to describe the relationship between a dependent variable, in this case the NO_3^- concentrations.

measured by Spectroquant Cell Test, and the independent variables. NO_3^- concentrations measured by ISE was performed both in raw samples and after added silver sulfate. The NO_3^- concentration in water samples ranged from 0.2 mg/L to 17.7 mg/L.

Backward elimination (BWE) was performed on results obtained by the multiple regression analysis (Table 9). Variables with $p > 0.05$ were eliminated. The relationship between concentrations from Spectroquant Cell Test and the independent variables ISE, pH, alkalinity and conductivity showed significance for all variables, hence there exist a connection. In contrast, the multiple regression analysis where ISE were added silver sulfate, showed a connection of ISE and conductivity with Spectroquant Cell Test. pH and alkalinity were eliminated.

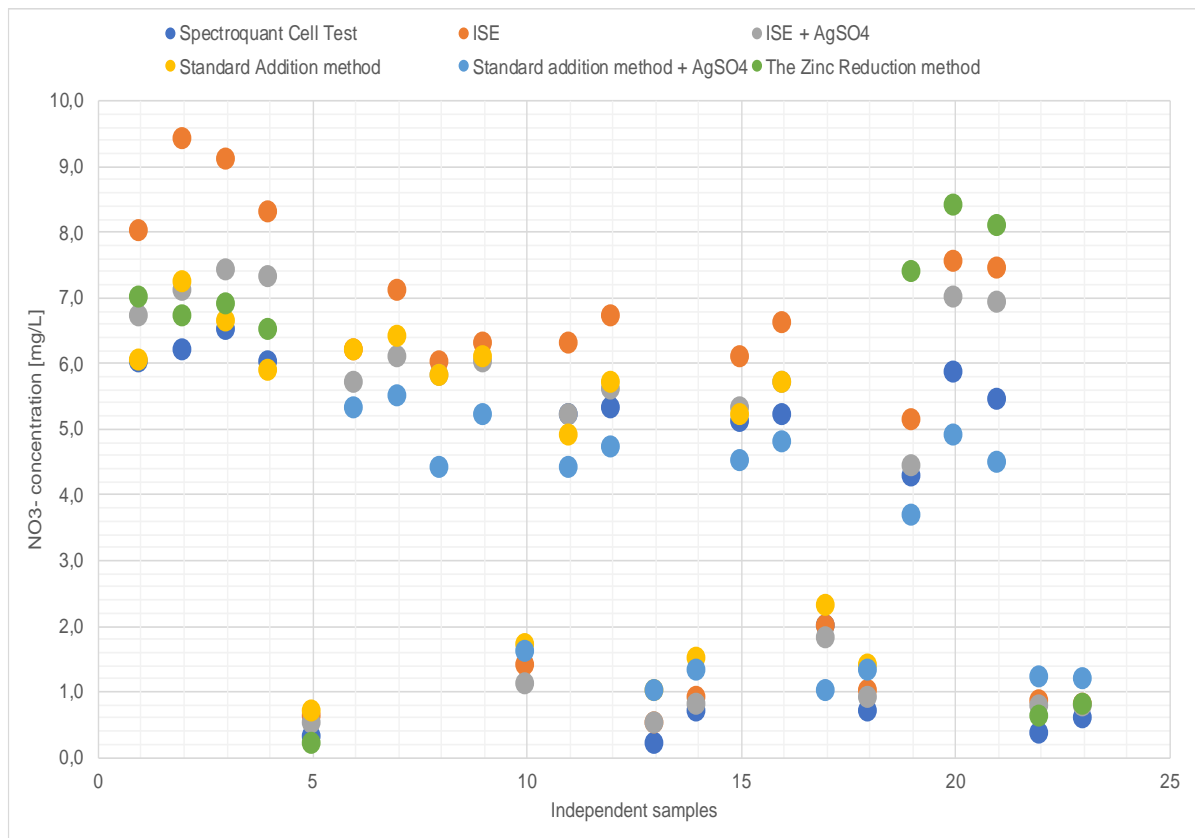


Figure 4-24 The result of 23 independent samples analyzed by Spectroquant Cell Test (dark blue), ISE with (grey) and without added silver sulfate (orange), The Standard Addition method with (light blue) and without added silver sulfate (yellow), and The Zinc Reduction method (green).

Additional methods for determining NO_3^- were included for comparison purposes. 23 independent samples measured by the additional methods are presented in

Figure 4-24 to visualize the large discrepancies between methods. Larger distances between points are observed at higher concentrations. The results from ISE is on average highest while The Standard Addition method is lowest. The result of NO_3^- measurements of different methods on samples taken 10th of April 2019 is presented in Figure 4-25.

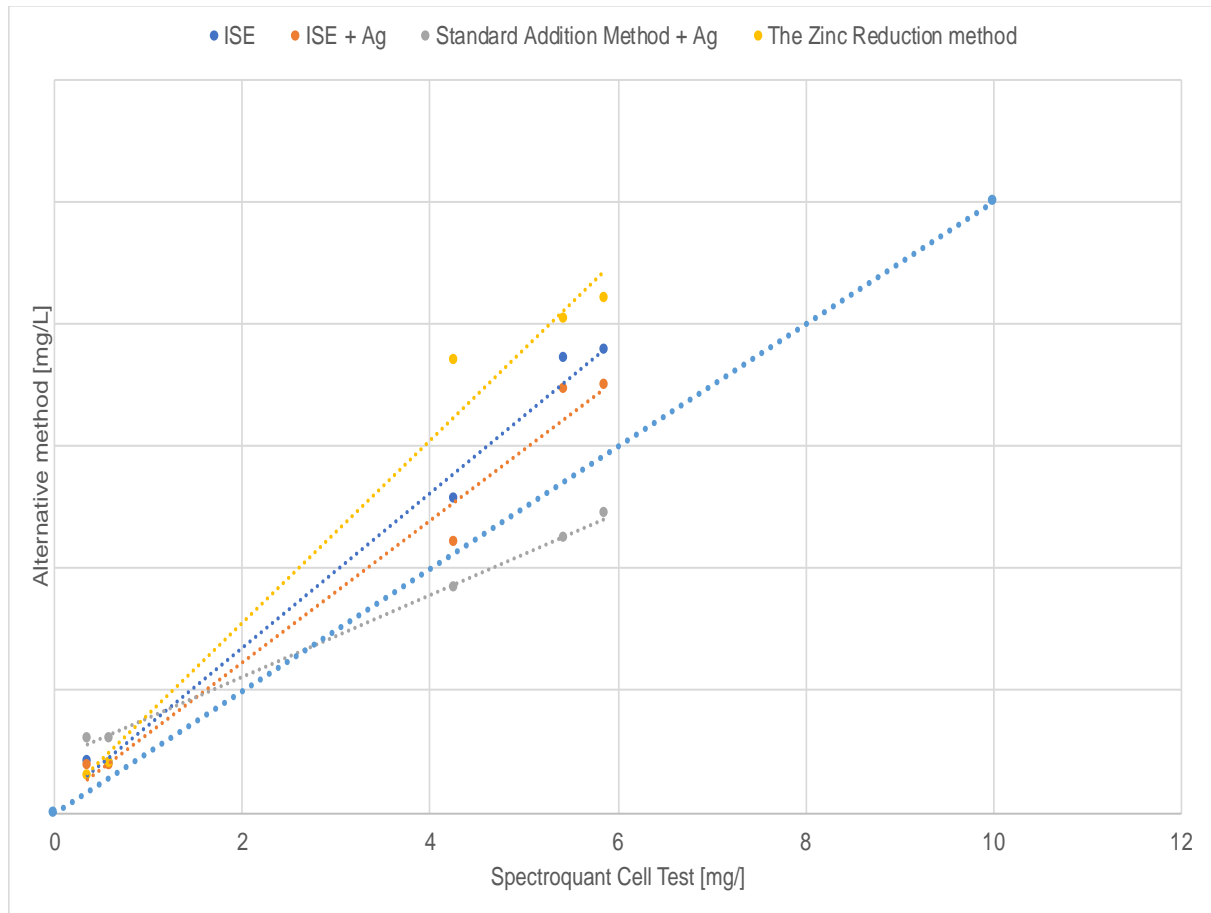


Figure 4-25 The result of NO_3^- measurements in water samples by different methods. Samples taken 10th of April 2019.

5. Discussion

A discussion of the results obtained during thesis and the methods used are presented in this section. The section is further divided into four sub-sections discussing the different aspects: (1) Nitrogen retention in Leikvollbekken, (2) Methods for determining nitrogen concentration, (3) Errors and uncertainties and (4) Suggestions for future research and improvements.

5.1 Nitrogen retention in Leikvollbekken

Constructed wetlands can be considered a black box where the system description is based on in- and outflow values (Bayona, 2018). The estimation of nitrogen retention in Leikvollbekken is based on nitrogen mass fluxes in and out of the wetland. The inside of the black box represents mechanisms involved in processes retaining nitrogen and their unknown rates, hence this approach is not suitable to investigate retention mechanisms in detail.

5.1.1 Long-term monitoring.

An overall positive retention efficiency of 9.4% (68.6 kg removed in the sampling period) TN was observed in Leikvollbekken in a 21-week period. The retention of the wetland was not estimated for the entire study period due to the installation of inlet sampler in December. However, outlet concentrations were measured throughout the thesis period.

The TN concentrations in inflowing water were in average 3.4 mg/L TN lower compared to the concentration at 11 mg/L (Løvhøyden, 1994) measured prior to the construction of the wetland in 1993/1994. This may be a result of monitoring the wetland for a relatively short period during this thesis, thus seasonal variations and fertilizer routines were not included. The lower average TN concentration compared to previous data may also be a result of the sampling method used. Before the construction, sampling procedure consisted of grab samples and not composite samples. The effect of the use of different sampling routines are presented in 5.3 Error and uncertainties.

The calculated retention efficiency of the wetland was an estimation of the wetlands ability to retain and remove nitrogen, through various processes such as nitrification-denitrification and plant uptake. The retention efficiency was estimated by dividing the total mass (kg) retained of the nitrogen compound considered, by the mass inlet. Hydraulic rate and nutrient concentration depend on precipitation, runoff conditions, seasonal activities, fertilizer routines and climate.

Excessive nitrogen input is mainly due to fertilizers added in the fields upstream the wetland, increase the concentrations significantly. The mass retained was based on the concentrations measured at two different locations in the same period, thus an indication of how much nitrogen entering and leaving the wetland in that specific period. As a consequence, higher nitrogen load in inlet water samples compared the estimated mass retained in a short period result in a lower retention efficiency and may not give a correct estimation of the actual retention performed by the wetland.

The flow rate in a wetland is vital when investigating the mechanisms for nitrogen retention and removal. Previous study (A.-G. Blankenberg et al., 2008) showed that the retention rate of TN can have large variations over year periods due to the variation in received hydraulic load. Higher hydraulic retention time (HRT) allows nitrogen compounds to be taken up by plants or contribute in other removal processes. Consequently, high hydraulic load decreases the HRT resulting in less removal of nutrients. During the monitoring period, no connection was found by regression analysis of TN retention and average flow. In periods with high flow (>100L/s) do water bypass mid-pond pipeline and pond 2, flowing directly to outlet. This is due to limiting capacity of the pipeline connecting the two ponds (Luth-Hanssen, 2018). Consequently, water is transported directly into Store Stokkavatn.

Soluble nitrogen constituted a large fraction of the TN concentration (up to 68%) in weekly water samples. The large fraction of soluble nitrogen in TN is a result of the high concentration of NO_3^- . TSS concentrations were measured to investigate if TN or particulate TN had a correlation to particles present in the water samples. A connection between TSS and particulate TN retention could indicate nitrogen adsorbed to particles. Hence particle sedimentation could be a nitrogen retention mechanism. The retention efficiency of TSS were estimated to 67% (1121.2 kg retained in the sampling period). The regression analysis showed no significant correlation between particulate TN and TSS.

The removal efficiency of NO_3^- and NH_4^+ were 6.1% (33.8 kg removed in the sampling period) and 87.1% (7.2 kg retained in the sampling period), respectively. In general, higher concentrations and larger variations were measured in inlet compared to outlet samples, indicating that nitrification-denitrification process and/or uptake may have occurred. The NH_4^+ removal (%) was relatively high compared to the other nitrogen parameters, mainly due to the low values measured. Average NH_4^+ concentration was measured to 0.1 mg/L and highest to 0.45 mg/L, which was significantly lower than the expected value of effluent after the construction of the constructed wetland at <1.0 mg/L (Bakke, 1993). Regression analysis

showed significant correlation between the increasing retention of NO_3^- and NH_4^+ against TN, separately.

In the period 5th of October until 1st of November 2018 a clear decline in concentration of NO_3^- and TN were observed in mid-pond and outlet samples (*Figure 4-5*). Inlet sampling equipment was not installed in this period, thus no data exist to confirm whether this was the case for inlet water samples. Precipitation and high hydraulic load may result in lower concentration at sampling locations due to dilution (Hessen, 2010), under the assumption that no excess nutrients from surrounding areas were washed out by precipitation. However, the dilution effect does not necessarily imply that the total transport of nutrients into the wetland may decrease.

The distinct peaks followed by weeks with lower positive retentions (*Figure 4-6*) may be a result of increased nitrogen concentrations into the wetland during high flow. In the period from 3rd of April the highest concentrations were observed in the mid-pond samples, followed by outlet and inlet (*Figure 4-3* to *Figure 4-5*). This is clearly observed as a negative retention in a period with relatively low average flowrate in *Figure 4-6* combined with increasing temperature (*Figure 3-6*). A hypothesis is that excess nitrogen comes from additional sources than through the inlet. The “oily” surface observed over a longer period in Pond 1 (*Figure 3-4*) is pointed out with a red dot in *Figure 5-1*. The grab sample taken 20th of February showed high NH_4^+ -concentration compared to other samples. A former compost heap is located in the elevated area marked in red (Roald Kommedal, pers. comm.). Inflow from compost heap may follow the drainage ditch ending in Leikvollbekken. Mineralization of organic material result in formation of NH_4^+ under a range of temperatures, moisture contents, pH levels and a diversity of microorganisms (Lee et al., 2009; Widowati et al., 2018); explaining the relatively high NH_4^+ concentration measured to >3.0 mg/L, and the low NO_3^- concentration of 0.6 mg/L. A high alkalinity (3690 $\mu\text{mol/L}$) was measured in the grab sample. A study (Abril & Frankignoulle, 2001) showed a strong correlation between high alkalinity and NH_4^+ , and low NO_3^- concentration and oxygen. This phenomenon seemed to also be the case here. Nitrification of NH_4^+ may be a reason for the increased NO_3^- and TN concentrations measured downstream. The lower concentration in outlet samples compared to mid-pond samples may indicate assimilation or denitrification process in Pond 2.



Figure 5-1 The red marked area illustrates area earlier used for compost deposition. The arrow points at potential runoff from the area down the drainage ditch leading to Leikvollbekken. The red point is where the grab sample was taken.

The pH was expected to be higher in outlet compared to inlet water samples from Leikvollbekken (Appendix J). Photosynthesis shift the carbonate-bicarbonate-carbon dioxide equilibrium to a higher pH by the utilization and production of carbon dioxide and oxygen, respectively (R.H. Kadlec et al., 1995). pH values in inlet and outlet water samples alternated at being highest in a fluctuating manner (Figure 4-9) indicating biological and chemical processes may have occurred in the sampling container. Moreover, this could include processes changing the composition of nitrogen compounds present in the sample. According to Standard Methods 4500-A (Clesceri et al., 1998) should pH be measured within a few hours. Weekly composite water samples were not measured for several days as the sampling lasted for longer periods. Therefore, pH values were not considered strictly stable. However, large variations in pH may lead to reduction or inhibition of nitrogen processes if the pH values increase or decrease beyond the range where the bacteria can no longer perform.

Alkalinity is affected by the nitrogen conversions in a wetland, as nitrification requires adequate buffering (Robert H. Kadlec et al., 2008). Alkalinity tended to have a relatively stable values throughout the sampling period and no significant correlation with nitrogen compounds was found. Hence, nitrification and other biogeochemical conversions processes were not likely affected by pH. In contrast, changes in conductivity showed a significant correlation with TN.

Lower conductivity measured in water samples is a good indication of dilution, which was clearly seen in Figure 4-3 and Figure 4-10. The conductivity played a significant role in the use of ISE (5.2 Methods for determining nitrate concentration).

Spreading of livestock manure is not permitted in the period 1st of September to 15th of February, neither in periods with frozen ground and snow cover to avoid excess runoff according to Norwegian regulations (Landbruksdepartemanget & Miljøverndepartemanget, 2002). Retention mechanisms and efficiency in constructed wetlands are dependent on temperature and nitrogen supply. Therefore, higher removal efficiency of TN are expected in summer months than in winter (A.-G. Blankenberg et al., 2008; Maltais-Landry et al., 2009). The Monitoring of Leikvollbekken in the period October 2018 until May 2019 was therefore not considered good enough documentation to estimate the annual retention of nitrogen compounds.

Reference samples from Store Stokkavatnet and Madlabekken showed lower concentrations (Figure 4-23) compared to samples from Leikvollbekken. The average TN concentrations in inlet, mid-pond and outlet samples in Leikvollbekken were in average 7.4 mg/L, 6.0 mg/L and 6.2 mg/L, respectively. Reference samples had an average concentration of 2.0 mg/L, implying that Store Stokkavatn receives significantly higher concentrations through Leikvollbekken. A comparison study of outlet concentrations in 1994 with measured concentrations in 1988/89 was performed after the construction. The comparison study showed a reduction in the outlet TN concentration of 22% (Løvøyden, 1994). The reduction in TN concentration observed during the monitoring period in this thesis was estimated to approximately 16%, which is close to the reduction in the study. However, different sampling procedures were performed, thus it is uncertain whether these numbers can be compared.

5.1.2 Storm event

Wash-out of nutrients and particles are expected during storm events. The observed storm event took place after a 23-day dry period. Close to zero precipitation combined with increasing temperature resulted in an average flowrate of 3-4 L/s the days before, while the highest flowrate during the storm event was measured to approximately 30 L/s. The storm event was relatively short and with low flow compared to previous periods where flow could increase > 100 L/s (Krahner, 2017; Luth-Hanssen, 2018).

Distinct concentration peaks of nitrogen compounds were observed close to the flow peaks (Figure 4-12). A significant correlation was found between TN concentrations and increasing average flowrate (Table 7.) TN concentration in water samples increased up to almost 600% compared to the concentration in sample prior to the storm event. An overall positive retention efficiency of TN (4.5%), NH_4^+ (13.1%) and TSS (6.0%) was measured (Table 6). In contrast, NO_3^- had a negative retention of -10.7%. The negative retention of NO_3^- was expected according to the “piston effect.” The “piston effect” states that precipitation in the recharge area of a basin causes pressure on the aquifers, which directly affects their discharge into rivers (Vasconcelos, 2017). This can be assumed for water-soluble nitrate in a wetland system. Nitrate hidden in pores and between sediments and plants may be displaced at higher flowrates.

In addition to the total retention the individual retentions in Pond 1 and Pond 2 were calculated. An interesting finding was that Pond 1 showed a negative retention for nitrogen compounds and positive retention for TSS, while Pond 2 was the opposite. Measured retention during such short storm event (24h) is the differences in the mass fluxes estimated between inlet, mid-pond and outlet of the wetland, thus not an indication of the actual nitrogen retention due to nitrogen processes and plant uptake in this period. No significant correlation was found between TN and TSS concentrations.

The negative retention in Pond 1 and positive retention in Pond 2 matches the pattern seen for weekly water samples in the period of negative retention (Figure 4-6). Concentrations in the mid-pond samples were higher than inlet and outlet. The reason may be contributions from areas previously not covered with water, decomposed plants or the compost heap. High water-level covering a larger area may cause the water to carry nutrients that would not otherwise be transported with the flow, such as the relatively quiescent area where the grab sample was taken. This may also explain the highest measured NH_4^+ concentration in a mid-pond sample at 2.7 mg/L compared to the highest concentration in an inlet samples at 1.17 mg/L.

Wash-out situations can be expected during storm events due to the higher flow velocity transporting more particles and nutrients compared to low flow conditions. However, the particle and nutrient concentrations washed out depends on the presence of the same nutrients in the catchment area affected by precipitation. This can be clearly seen for TN and TSS concentrations for inlet samples (Figure 4-14 and Figure 4-18). TN and TSS was measured to 13.0 mg/L and 106.2 mg/L in the first peak, respectively. In the second peak the concentrations for TN and TSS were 14.2 mg/L and 35.8 mg/L. Moreover, the second flow peak was 209% higher than the first peak. Higher flow over time does not necessarily mean continuously high

input of nutrients to the wetland but rather result in a rapid initial concentration surge (wash-out) followed by a limited pulse more dominated by dilution.

Dilution of the water in the wetland led to a clear observed reduction in pH, alkalinity and conductivity (Figure 4-20 and Figure 4-21). However, the change in pH, alkalinity and conductivity are not considered having a large effect on the nitrogen removal efficiency in the longer period, as these relatively “small” storm events occur frequently. As seen in the period after the storm event (Figure 4-9 and Figure 4-10) did these parameters recover to initial value. However, conductivity is used as a measure of the amount of dissolved salts in the water. A significant correlation between TN and conductivity was found, both in samples during weekly monitoring and during storm event. Changes in the ionic strength of the water and may mobilize adsorbed ions in soil and sediments, both in the catchment area and in the wetland, in periods with heavy precipitation (K, Roald. Pers. Comm.).

A significant correlation was found between TN and color, which could indicate TN present in humus. Color in water samples increased up to 796% compared to the samples prior to storm event, with highest concentration measured in a mid-pond sample during the third flow peak (Figure 4-21). This indicates leaching of humus-containing substances, colloids and exchange of ionic organic components (Kommedal, R. Pers. Comm.), thus during high flow may wetlands have higher nitrogen input due to nitrogen present in humus (Ødegaard & Norheim, 2014).

5.2 Methods for determining nitrate concentration

Two different methods for determining nitrate concentration in samples were used throughout this thesis. Weekly samples were analyzed by Spectroquant Cell Test and ISE Nitrate Electrode, while storm event samples were only analyzed with electrode. Differences up to 3.2 mg/L between the methods were discovered Figure 4-24.

Although the ISE is characterized by fast response, near theoretical sensitivity and high selectivity for nitrate ions, may interferences occur. Potential ions (with selectivity constants) that may interfere with the electrode are by the manufacturer reported to be Cl^- ($K=0.006$), NO_2^- ($K=0.1$), BR^- ($K=0.16$), ClO_3^- ($K=2.5$) and I^- ($K=15$). For comparison, the Spectroquant Cell Test used is not suited for determination in waters exceeding 1000 mg/L Cl^- .

Precipitation of silver chloride was observed in samples from Leikvollbekken and reference samples, indicating the presence of chloride ions (Figure 4-22). By adding silver sulfate to

samples did the average concentration measured decrease approximately 9.4% lower compared to using ISE directly. An additional observation was the time the electrode used to stabilize when no silver sulfate was added, which was longer compared to with the additive. Interference by NO_2^- in water was assumed to be non-significant.

Due to deviations between ISE and Spectroquant Cell Test were the Zinc Reduction method and Standard Addition method included. In general, for higher concentrations did the ISE and Spectroquant Cell Test differ the most. In a comparative study of different techniques for nitrate determinations (Raikos, Fytianos, Samara, & Samanidou, 1988) was it concluded that The Cadmium Reduction method was most suitable for environmental water samples as electrodes are easily interfered by other ions. However, this is a relatively old study and electrodes have improved. In Figure 4-24 (right) do the Zinc Reduction method deviating more than ISE.

According to the Cadmium Reduction in Standard Methods (Clesceri et al., 1998) are the applicable range 0.01 to 1.0 mg NO_3^- -N/L. ISE and the Zinc Reduction method was performed on “clean” water samples collected from the oligotrophic lake Vikastølsvatn (Espen Enge, pers. comm.) The two methods showed no significant difference ($p > 0.05$) (Appendix F). In the case of samples from Leikvollbekken, large uncertainties are introduced as the samples are highly diluted in order to be measured by this method. Dilution and the potential of interference ions in the samples may be the reason why the results by this method is differing from the other methods.

The Standard Addition method was performed using the same ISE. In general, the results were higher for low NO_3^- concentrations and lower for higher concentrations compared to the other methods (

Figure 4-24). The method was tested by performing it on samples with known concentrations. The results did not correlate with the known concentrations, thus not considered reliable. The reason is not known and need further research.

Multiple regression was performed on the water samples to describe the relationship between a dependent variable, in this case the NO_3^- concentrations measured by Spectroquant Cell Test, and the independent variables. NO_3^- concentrations measured by ISE was performed both in raw samples and after added silver sulfate. The result indicated that the presence of interference ions plays a factor in the relationship between Spectroquant Cell Tests and ISE Nitrate Electrode. The result of BWE (Table 9) formed the basis of Equation 9 used to convert measured NO_3^- concentrations by ISE to Spectroquant Cell Test in storm event samples. A

comparison of a range of concentrations measured by Spectroquant Cell Test, ISE and concentrations calculated from Equation 9 is presented in Appendix H. It is important to point out that the range Spectroquant Cell Test is 1.0-25.0 mg NO₃⁻/L. Nitrate concentrations lower than 1.0 mg/L presented in results are estimated from calibration curves and should not be considered the correct value but rather < 1.0 mg/L.

5.3 Error and uncertainties

A wide range of potential errors and uncertainties are relevant for the thesis. Sampling procedures, laboratory work and interpretation of results do all introduces factors that may affect the final presented results.

Inlet and mid-pond sampler were programmed for time-proportional sampling, while outlet sampler was set for flow-proportional sampling. Combining two different sampling methods introduces uncertainties into the calculation of mass fluxes and estimated retentions. Time-proportional samples were programmed to take 90 ml sample each hour and flow-proportional sampling were programmed to 50 ml samples every preset number of pulses. This may result in fewer measurements by the inlet sampler during period with high precipitation. Consequently, giving a non-representative amount of TSS and other parameters when compared to outlet sampling.

Time-proportional sampling may under- and overestimate the nitrogen concentration if greater peaks cause washout episodes with heavy precipitation. A potential consequence is that the results show a lower retention than what was actually achieved. However, a study of comparison of three different sampling methods in three Norwegian catchments (Haraldsen & Stålnacke, 2006), including flow-proportional composite sampling and time-proportional sampling, showed that differences in nitrogen load between the methods were smaller than for phosphorus or suspended solids. Total nitrogen had a smoother concentration pattern over the year and did not tend to have the same wash out peaks as phosphorus and particles, due to the high fraction of nitrate in TN being soluble (Audet et al., 2014). It is especially during flow events and when flow peaks are not predictable that time-dependent sampling tend to be inferior to catch phosphorus and particles. Due to these parameters are flow-dependent measurements considered more reliable measurements in dynamic streams affected by agricultural influx (Haraldsen & Stålnacke, 2006). Different settings for the automatic samplers during weekly samples led to different sampling frequency and volume. Under low flow did the flow-

dependent sampler sample less often, leading to smaller volume collected during the week and less variations detected over time. In contrast, the time-dependent samplers continuously sampled as the suction tube was totally submerged during the whole period.

During storm event were all three automatic samplers programmed with time-proportional settings, starting approximately at the same time. Four sub-samples were collected in each bottle, one each 15 minutes. By doing this, samples were covered by 15 minutes measurements and the introduced uncertainties by using two different settings were avoided.

Reference samples were taken as grab samples, collecting a small volume of water. Grab samples are simple and quick method. However, it has some disadvantages as it only represent a “snapshot” of the water’s geochemical composition in the precise moment when sampling is performed, not taking into consideration that the composition of nutrients and other components may change rapidly over time in the lake (Audet et al., 2014). In the case of sampling in Store Stokkavatnet, large variation in movement of the surface of the water was observed. Mostly the water was clear, but in cases of windy weather the particles from bottom sediments seemed to resuspend making the water much more turbid.

In February, vegetation started to prevent water to pass the submerged suction line at inlet. Increased vegetation may contribute to change in flow direction of incoming water or retain the water already present, causing non-satisfactory sampling of the water passing.

The standard deviation of NO_3^- , NH_4^+ and TN Spectroquant Cell Tests (Table 4) was estimated to 0.2 mg/L (1.3%), 0.004 mg/L (8.3%) and 0.2 mg/L (4.3%), respectively, which was relatively low. The standard deviation of NH_4^+ are almost twice as high as for TN and over six times higher compared to NO_3^- . The reason for this may be the low concentrations, often lower than detection limit for the method used. A standard deviation of 0.004 mg/L are really low compared to the standard error of 0.013 mg $\text{NH}_4\text{-N/L}$ and 0.021 mg $\text{NH}_4\text{-N/L}$ reported by the manufacturer, thus considered insignificant in this analysis. The R^2 value in calibration curves for NO_3^- and TN analysis was in average 0.9998 and 0.9980, respectively. In both analyses did the standard solutions used in calibration curves show a low variance, with an uncertainty of 0.02% for NO_3^- and 0.20% for TN. The largest uncertainty in TN analysis may be due to procedure prior to the Spectroquant Cell Test, such as during digestion and autoclave.

Human factors, such as contamination, errors in dilution of solutions or pipetting, may have contributed to standard deviations. The standard deviations estimated are based on three parallels analyzed from 5th of October 2018 to 13th of December, and not the entire sampling

period. The optimum would have been to continue with parallels in all tests performed throughout the thesis, to estimate a more accurate deviation.

Some of the parameters measured are temperature and time sensitive, especially the composition of nitrogen compounds and pH. In general, nitrogen compounds, pH and color were measured the same day as collecting samples. Alkalinity, conductivity and TSS/FSS were analyzed within one day after sampling. Samples were placed in a refrigerator if not all analyzes could be done in the same day as they were collected. This was applied in particular for samples collected during the storm event, as some of the parameters were analyzed several days later. All samples were supposed to have the same temperature, preferably room temperature, before analyzed. This may have influenced the results as the precise temperature was not measured.

5.4 Suggestions for future research and improvements

The main focus on nutrient retention in Leikvollbekken have previously been on phosphorus retention as it is the limiting nutrient for primary production in freshwater systems (Krahner, 2017; Luth-Hanssen, 2018). The wetland was expected to have a positive effect also on nitrogen removal through biological assimilation and dissimilation, hence it would be interesting to investigate if that is the case.

This thesis covers a study of nitrogen compounds entering and leaving the constructed wetland in the period of October 2018-May 2019, stating that changes in nitrogen mass fluxes have occurred in the period monitored. However, troubles with equipment led to an incomplete monitoring of the wetland and an inferior impression of the effect of the individual ponds. Monitoring of the wetland with regard to nitrogen retention over several months, in both ponds, should be performed including the warmer months not covered in this thesis to get a better impression of the annual nitrogen retention. Moreover, with regard to the storm event monitored, several samplings should be performed after the flow peaks to see how the concentrations varies further. This was unfortunately not performed on the storm event studied in this thesis. In future monitoring it should be used samplers with same settings to ensure more accurate comparison between the different sampling locations.

The degree of nitrogen uptake in plants depends on which plants are present in the wetland. In this thesis it has not been investigated which plants are present nor their nitrogen content. Since plant uptake is considered an essential removal mechanism of nitrogen compounds, could

management and estimation of plant species distributions and the uptake by plants contribute to develop the retention efficiency of this wetland.

Nitrogen retention is dependent on the hydraulic retention time as higher flow limits the function of retention mechanisms. Trace studies of the hydraulic flow should be performed to investigate if the wetland is properly designed for optimal retention efficiency. Further improvements of Leikvollbekken with regard to nitrogen retention includes regular maintenance including excavation to ensure better spreading of water and increasing hydraulic retention time, and reduce trees surrounding the area to increase the opportunities for sun. In addition, plant harvesting should be considered.

6. Conclusion

The water entering Leikvollbekken had significantly higher nitrogen concentration compared to Store Stokkavatn and Madlabekken. An overall positive TN retention of 9.4 % (68.6 kg) was observed in the constructed wetland in the period of monitoring (Dec. 2018- May 2019.) NO_3^- constituted a large fraction of TN (in average 83.2 % of TN) with an observed 6.1% removal efficiency. In contrast, NH_4^+ was measured to relatively low concentrations, often under detection limit of the method used. The observed removal efficiency was 87%.

Concentrations of nitrogen compounds varied with flow throughout the period. However, no correlation between nitrogen retention and average flowrate was found. Nitrogen concentrations in water samples collected during storm event exceeded the concentrations measured during weekly sampling. A clear negative retention was observed in April and May for weekly measurements in a period of zero precipitation and increasing temperature. The same pattern was seen in Pond 1 during the storm event. This was believed to be a result of contribution of other nitrogen sources than incoming water, potentially contribution from a compost heap near Pond 1 or other nitrogen sources in the wetland.

Does the mature constructed wetland play a significant role in reduction of nitrogen compounds to the recipient? Based on data obtained during this thesis the answer is yes, but to a small extent. Due to a relatively short monitoring period, different sampling setups and lack of data due to equipment issues, more research are needed to provide a more complete answer to that question.

7. References

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Appendix

- APPENDIX A: Chemicals and solutions used in analytical methods
- APPENDIX B: Calibration curves used to calculate NO_3^- and TN concentrations
- APPENDIX C: Monthly weather data for Thesis period and detailed precipitation data from storm event
- APPENDIX D: Variation in inlet, mid-pond and outlet concentrations for NO_3^- , TN and NH_4^+ in weekly water samples.
- APPENDIX E: Mass fluxes for NO_3^- , NH_4^+ and TN in weekly water samples and storm event samples
- APPENDIX F: Comparison of Ion-Selective Electrode and the Zinc Reduction method
- APPENDIX G: Statistical analysis and scatterplots of weekly water samples and storm event samples
- APPENDIX H: Recalculation of ISE NO_3^- values
- APPENDIX I: Information board at site
- APPENDIX J: Previous data from Leikvollbekken
- APPENDIX K: pH, conductivity, alkalinity and color in reference samples

APPENDIX A: Chemicals and solutions used in analytical methods

Table 10. Chemicals and solutions, their quality and purpose in thesis

Solution	Chemicals	Quality and producer	Purpose
ISA	0.2M KH ₂ PO ₄ + NO ₃ ⁻ -N 0.25 mg/L	PA-grade, VWR Chemicals	ISE Nitrate Electrode
AgSO₄	1.6 mg AgSO ₄ → 200 ml	PA-grade , Alfa Aesar	ISE Nitrate Electrode
Digestion reagent	2.0 g K ₂ S ₂ O ₈ + 0.3 g NaOH → 100 ml	PA-grade, Merck	Standard methods 2500-D
Buffer solution	61.8 g H ₃ BO ₃ + 8.0 g NaOH → 1000 ml	PA-grade, Merck	Standard methods 2500-D
NO₃- Stock solution	100 mg/L NO ₃ ⁻ N	PA-grade, Merck	Standard solutions used in ISE and Spectroquant Cell Tests.
H₂SO₄	0.01 M H ₂ SO ₄	PA-grade, Merck	Alkalinity

APPENDIX B: Calibration curves used to calculate NO₃⁻ and TN concentrations

An example of a calibration curve obtained from standard NO₃⁻ solutions of 1, 5 and 10 mg/L for Spectroquant Cell Test is given in figure B-1. New calibration curve was made for each time the analysis was performed. The same standard solutions were used for determining TN concentrations, by first autoclaving them. The curve shown in the figure, with slope of 17,579 and intercept of 0,0127 was used to calculate the unknown concentration 21st of March 2019.

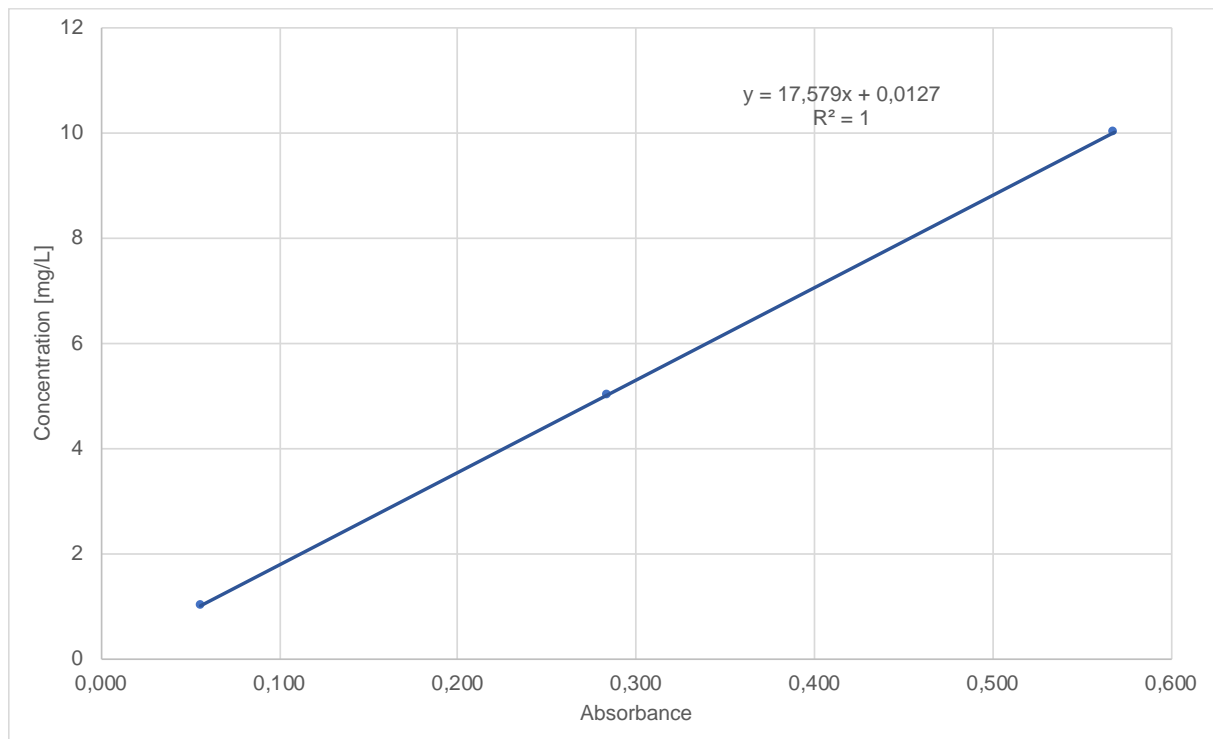


Figure B-1 Example of calibration curve used in NO₃⁻ analysis by Spectroquant Cell Tests (21st of March 2019).

Same principle was used to determine NO₃⁻ concentrations by ISE. Standard solutions of 1, 5 and 10 mg/L were used to create the calibration curves (Figure B-2) for each time the analysis was performed. The slope -0,0287 and intercept 8,1144 were used in Equation A-1 to calculate the unknown concentration 10th of April 2019. 0,25 mg/L was extracted due to added Ionic Strength Adjustor. The measurement was repeated two times for each analysis resulting in a trendline based on the mV for the six standard solutions.

$$NO_3^- \left[\frac{mg}{L} \right] = 10^{-mV \cdot a + y} - 0,25$$

Equation B-1

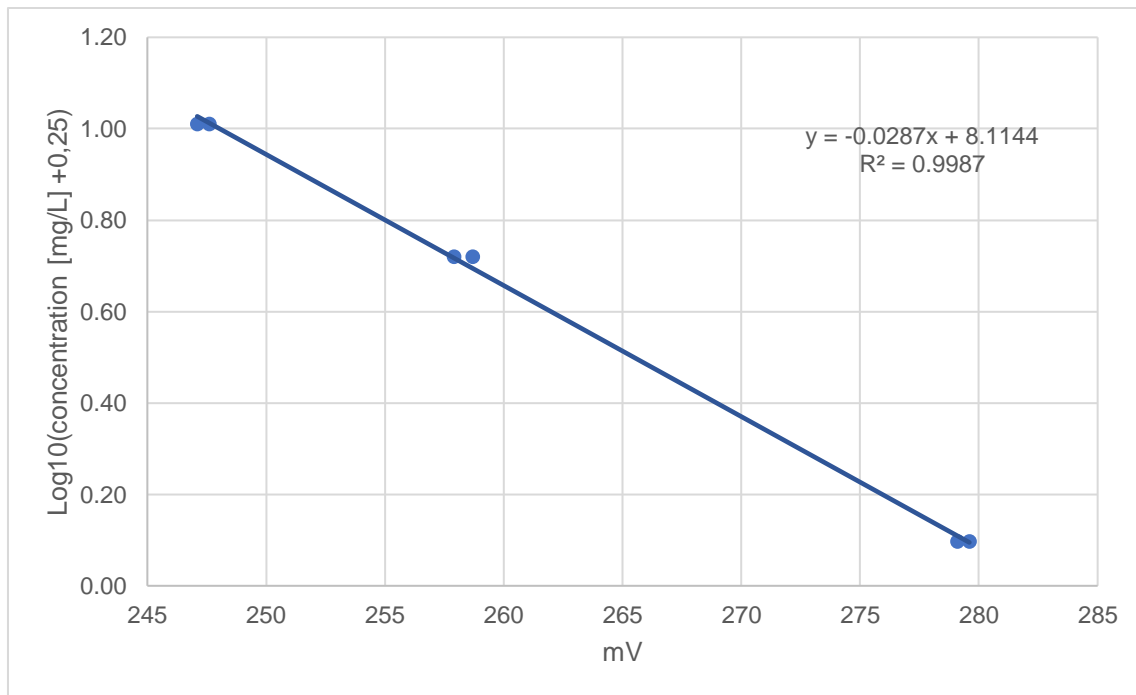


Figure B-2 Example of calibration curve used in NO_3^- analysis by ISE (10th of April 2019).

APPENDIX C: Monthly weather data for Thesis period and detailed precipitation data from storm event.

Table C-1: Monthly precipitation and temperature data in the period 1st of October to 13th of May (Meteorologisk institutt, 2007-2019).

Month	Precipitation [mm]		Temperature °C		
	Total	Highest	Average	Highest	Lowest
Oct-18	275.7	60.8	8.9	19.9	-0.1
Nov-18	68.1	9.7	6.6	14.8	-1.9
Dec-18	87.9	16.4	4.1	8.8	-1.6
Jan-19	85.2	18.2	2.5	7.9	-3.9
Feb-19	50.8	11.0	5.0	14.2	-2.8
Mar-19	169.7	13.7	4.7	11.5	-1.4
Apr-19	43.8	27.6	9.0	21.9	-1.1
May-19	22.7	10.8	6.1	10.6	0.5

Table C-2: Detailed precipitation data from storm event 26th – 27th of April 2019 (Meteorologisk institutt, 2007-2019).

Time	Precipitation [mm]
18:00:00	0.0
19:00:00	4.1
20:00:00	3.9
21:00:00	0.0
22:00:00	0.2
23:00:00	1.3
00:00:00	2.5
01:00:00	3.2
02:00:00	2.6
03:00:00	3.9
04:00:00	3.3
05:00:00	0.9
06:00:00	0.9
07:00:00	0.7
08:00:00	0.4
09:00:00	2.4
10:00:00	1.6
11:00:00	2.1
12:00:00	1.9
13:00:00	1.4
14:00:00	2.2
15:00:00	0.9
16:00:00	0.0
17:00:00	0.0
18:00:00	0.0

APPENDIX D: Variation in inlet, mid-pond and outlet concentrations for NO_3^- , TN and NH_4^+ in weekly water samples.

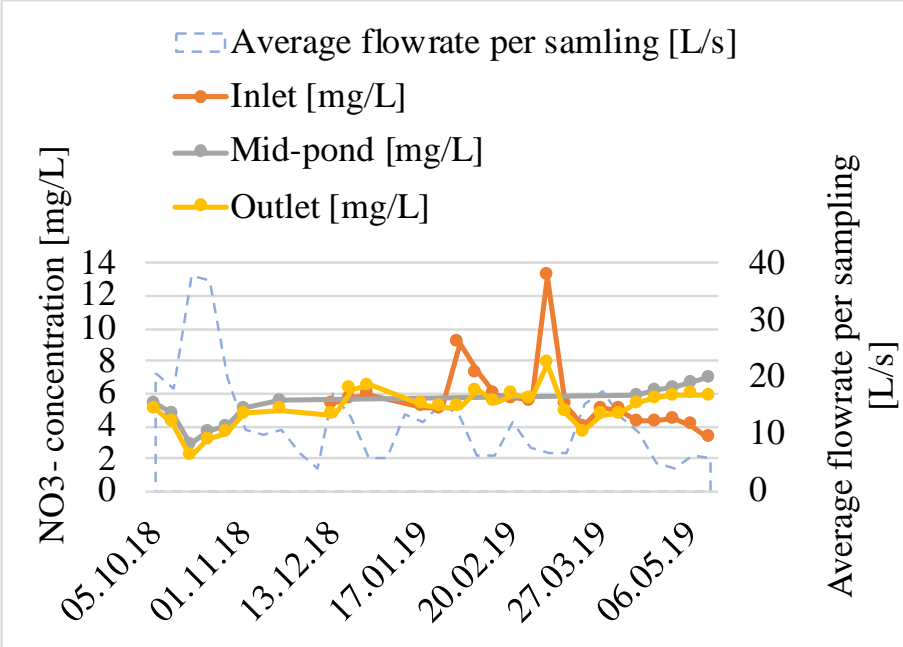


Figure D-1: Variations in inlet, mid-pond and outlet concentrations for NO_3^- .

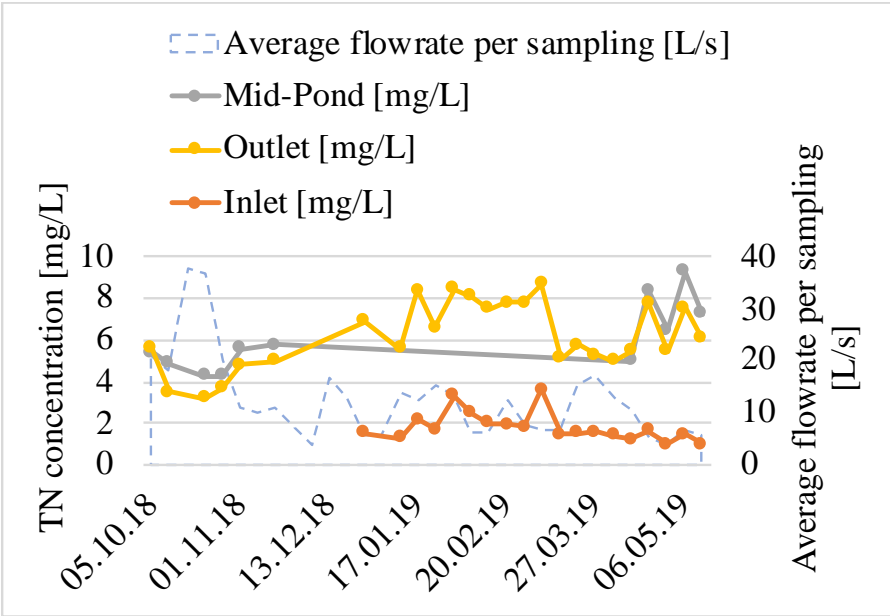


Figure D-2: Variations in inlet, mid-pond and outlet concentrations for TN.

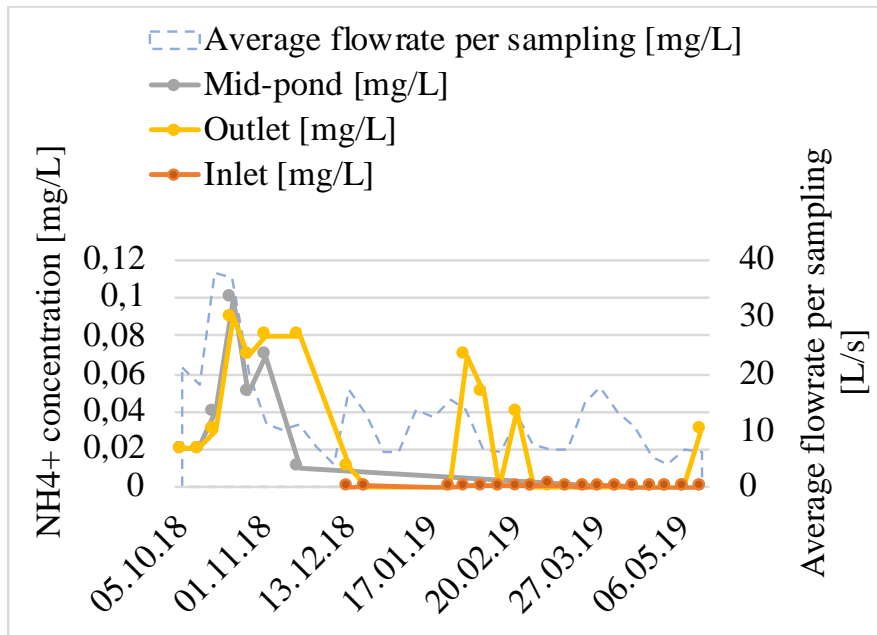


Figure D-3: Variations in inlet, mid-pond and outlet concentrations for NH_4^+ .

APPENDIX E: Mass fluxes for NO_3^- , NH_4^+ and TN in weekly water samples and storm event samples

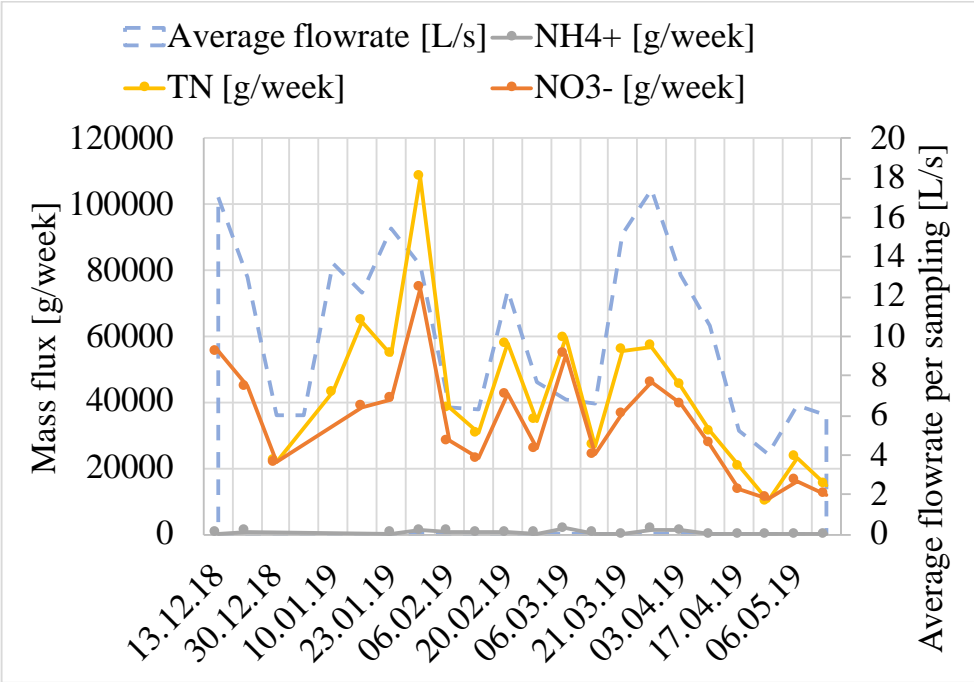


Figure E-1: Mass fluxes of NO_3^- , NH_4^+ and TN in inlet of Leikvollbekken.

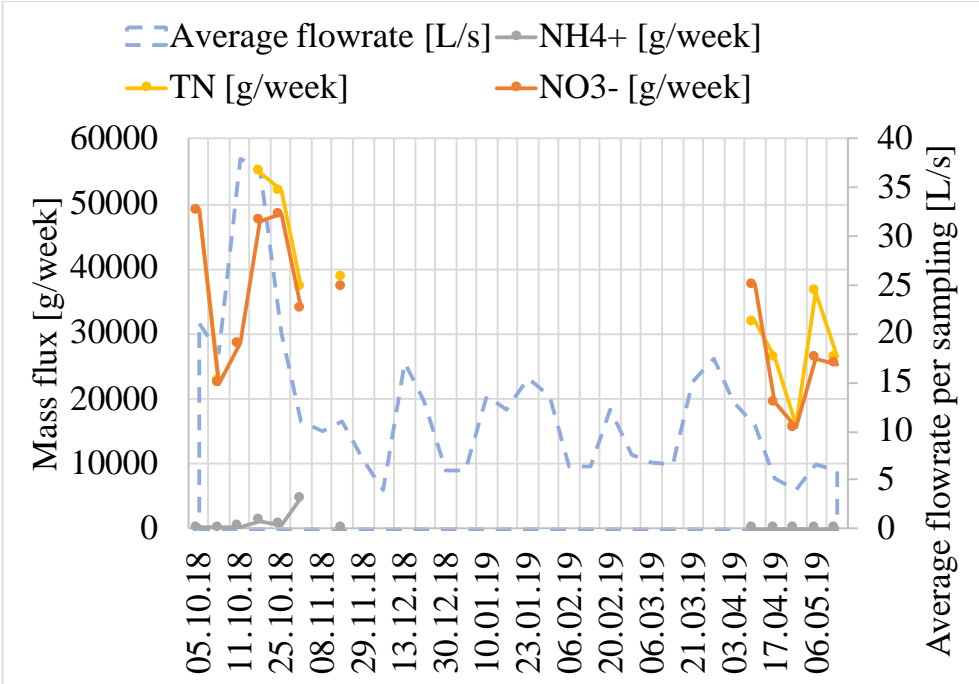


Figure E-2: Mass fluxes of NO_3^- , NH_4^+ and TN in mid-pond of Leikvollbekken

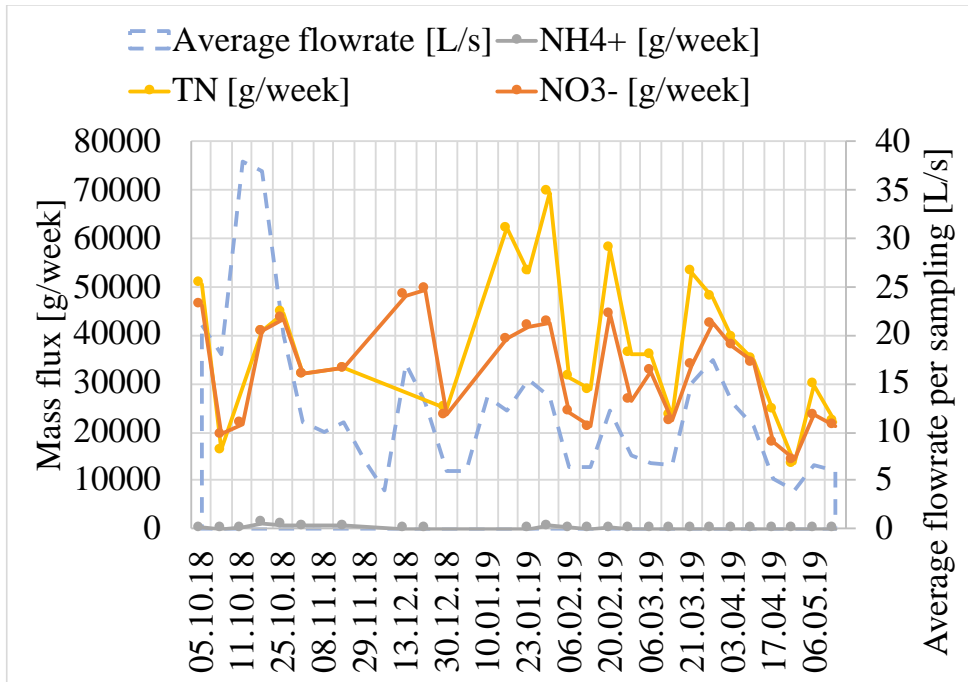


Figure E-3: Mass fluxes of NO_3^- , NH_4^+ and TN in outlet of Leikvollbekken.

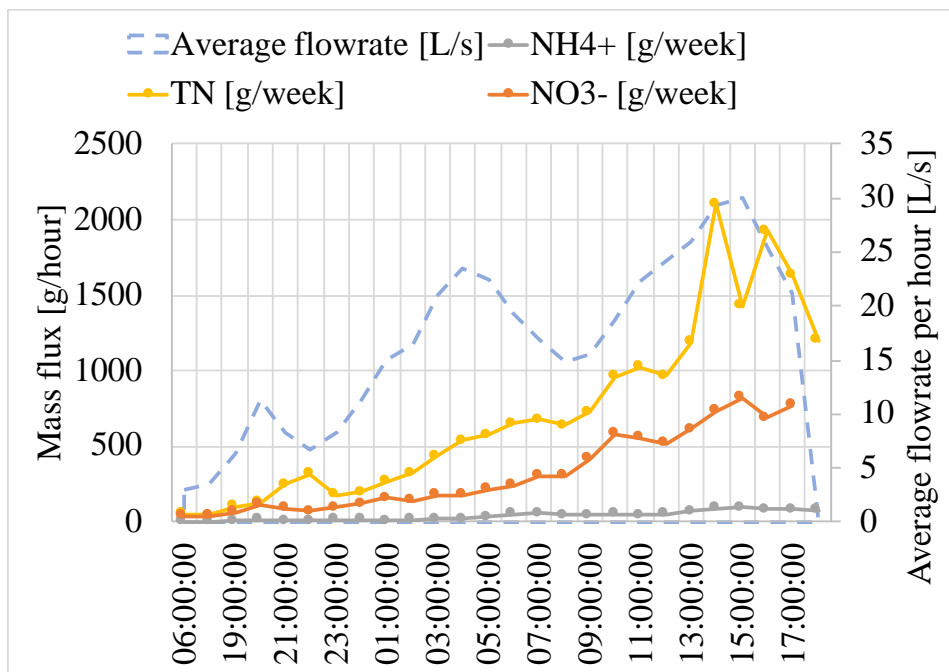


Figure E-4: Mass fluxes of NO_3^- , NH_4^+ and TN in inlet of Leikvollbekken during storm event.

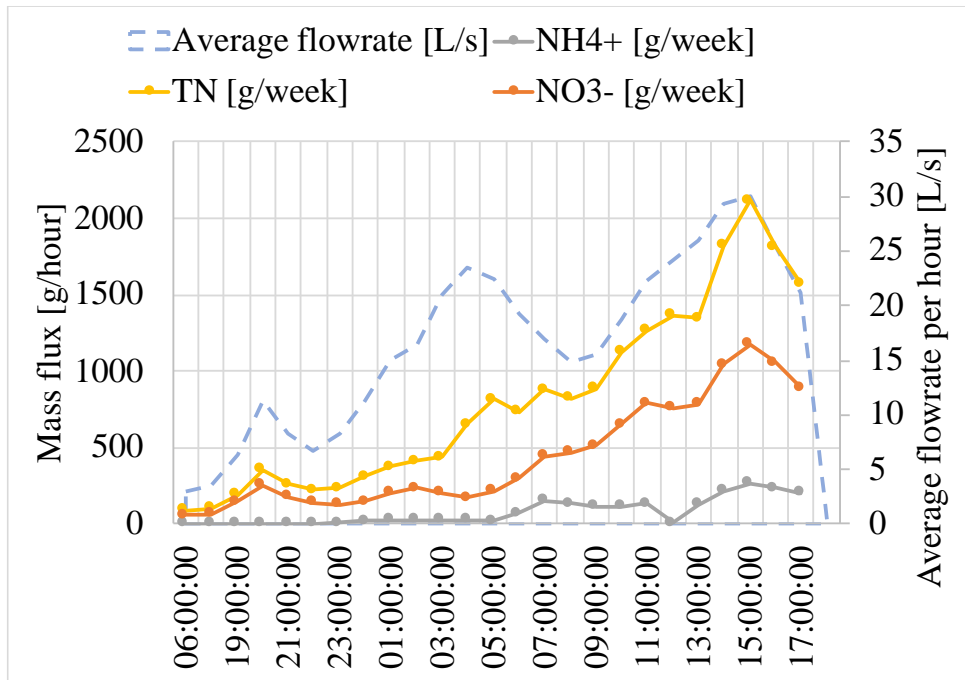


Figure E-5: Mass fluxes of NO_3^- , NH_4^+ and TN in mid-pond of Leikvollbekken during storm event.

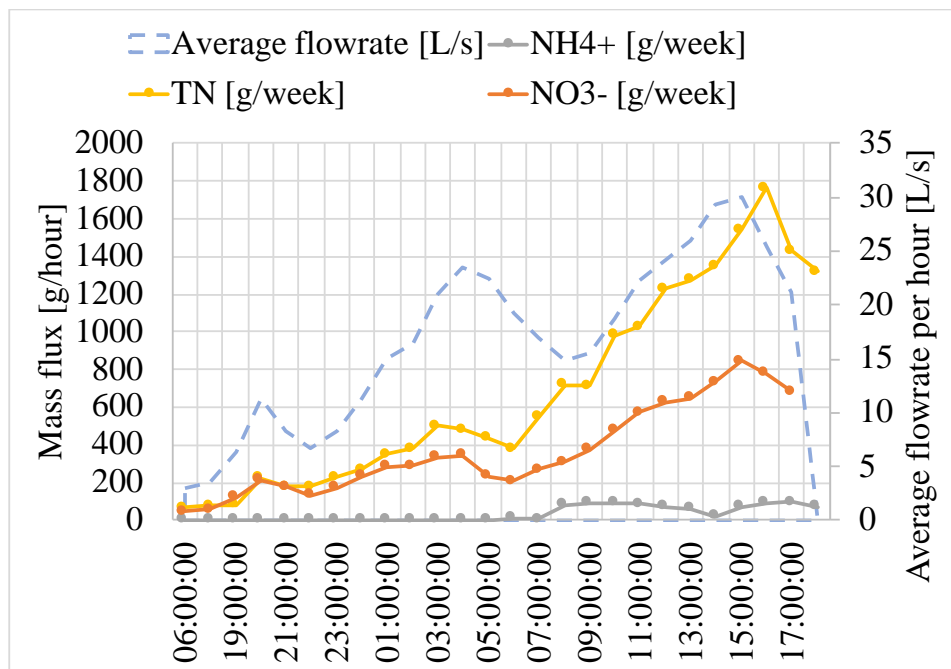


Figure E-6: Mass fluxes of NO_3^- , NH_4^+ and TN in outlet of Leikvollbekken during storm event.

APPENDIX F: Comparison of Ion-Selective Electrode and the Zinc Reduction method

“clean” water samples from the oligotrophic mountain lake Vikastølsvatn were analyzed for NO_3^- by ISE and the Zinc Reduction method to compare concentrations determined by the two methods. The samples were analyzed by Henrik van der Hoeven (Table F-1).

Table F-1: NO_3^- concentrations in water samples from Vikastølsvatn measured by Ion-Selective Electrode and the Zinc Reduction method.

Sample	Zinc Reduction method [mg/L]	ISE Nitrate Electrode [mg/L]
1	0.46	0.43
2	0.45	0.43
3	0.47	0.45
4	0.46	0.46
5	0.44	0.45

APPENDIX G: Statistical analysis and scatterplots of weekly water samples and storm event samples

Regression analysis performed on different parameters from weekly water samples (Table G-1) and samples collected during storm event (Table G-2). Scatterplots of significant correlations in thesis is presented in Figure G-1, Figure G-2 and Figure G-3.

Table G-1: Regression analysis on parameters from samples collected during weekly sampling.

Parameters	Coefficient	R²	p-value	n
NO₃⁻ [g/week] vs. Flow [L/s]	-0.11	0.06	0.202	28
NH₄ [g/week] vs. Flow [L/s]	<0.001	<0.001	0.993	28
TSS [kg/week] vs. Flow [L/s]	8.60	0.19	0.041	22
NO₃⁻ [mg/L] vs. TN [mg/L]	0.79	0.82	<0.001	28
NH₄⁺ [mg/L] vs. TN [mg/L]	0.04	0.58	<0.001	28
Particulate TN [g/week] vs. TSS [g/week]	<0.001	0.18	0.135	14
pH vs. Flow [L/s]	-0.01	0.08	0.155	28
Conductivity [μS/cm] vs. Flow [L/s]	-2.79	0.20	0.016	28
Alkalinity [μmol/l] vs. Flow [L/s]	7.73	0.11	0.087	28
Color [mg Pt/L] vs. Flow [L/s]	1.82	0.28	0.004	28

Table G-2: Regression analysis performed on parameters from samples collected during storm event.

	Parameters	Coefficient	R ²	p-value	n
Pond 1	pH vs. Flow [L/s]	0.00	0.24	0.013	25
	Conductivity [μ S/cm] vs. Flow [L/s]	-0.36	0.01	0.710	25
	Alkalinity [μ mol/L] vs. Flow [L/s]	-4.11	0.13	0.082	25
	Color [mg Pt/L] vs. Flow [L/s]	2.70	0.37	0.001	25
Pond 2	pH vs. Flow [L/s]	-0.01	0.60	<0.001	25
	Conductivity [μ S/cm] vs. Flow [L/s]	-2.31	0.20	0.023	25
	Alkalinity [μ mol/L] vs. Flow [L/s]	-20.32	0.68	<0.001	25
	Color [mg Pt/L] vs. Flow [L/s]	1.70	0.40	<0.001	25

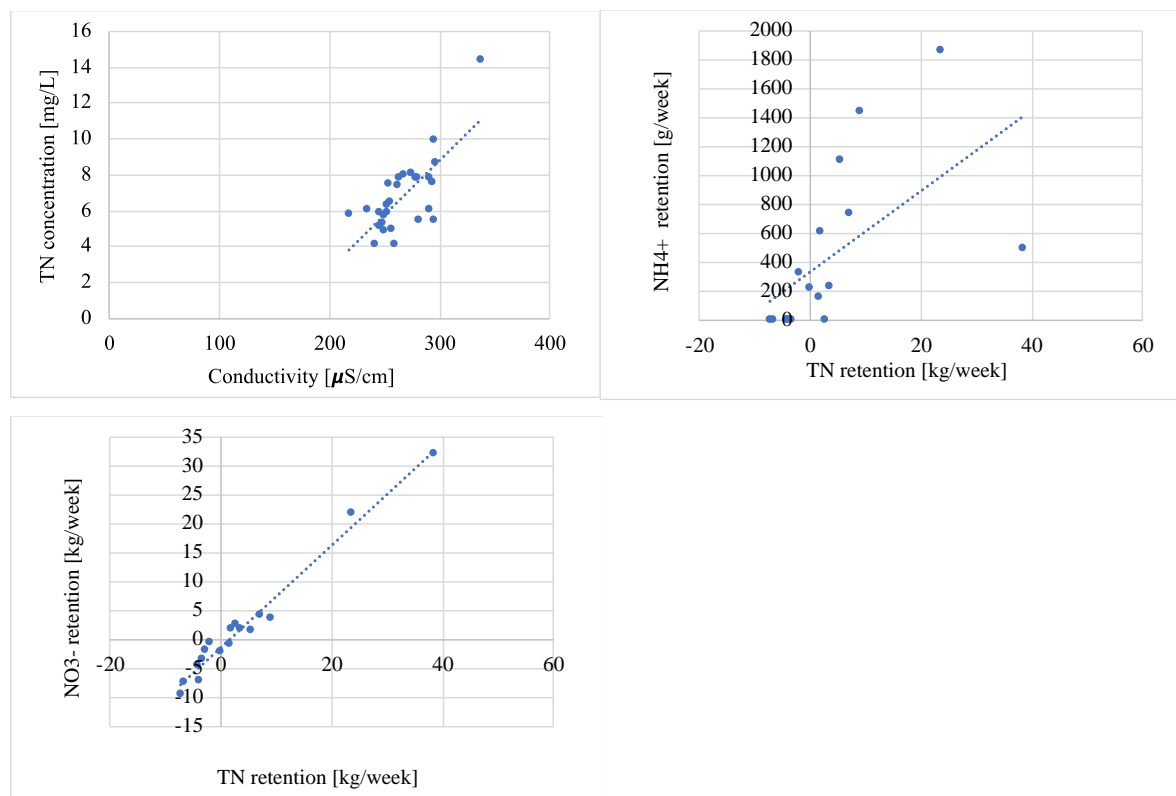


Figure G-1: Scatterplots of TN, NO₃⁺ and NH₄⁻ parameters measured in weekly water samples.

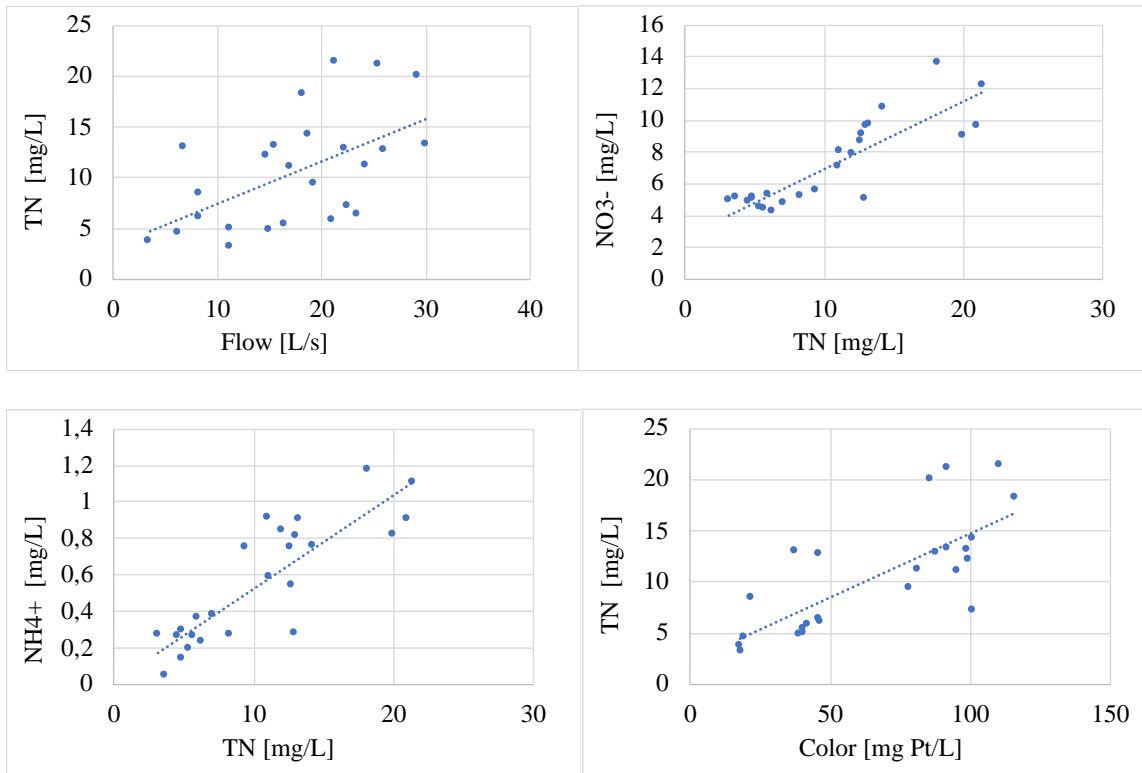


Figure G-2: Scatterplots of parameters measured in water samples in inlet of Pond 1 during storm event

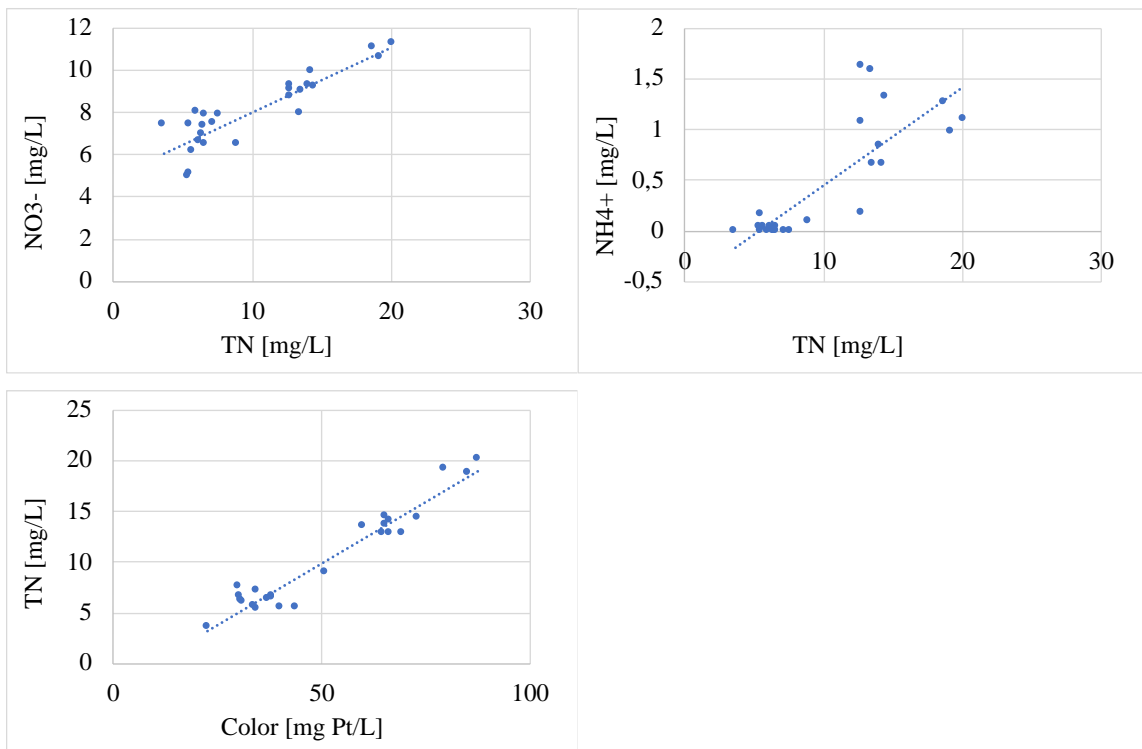


Figure G-3: Scatterplots of parameters measured in water samples in outlet of Pond 2 during storm event

APPENDIX H: Recalculation of ISE NO₃⁻ values

An excerpt of the test on ISE+Ag and Spectroquant Cell Test values against values adjusted by the regression line by equation: $y = 0.64 * ISE \left[\frac{mg}{L} \right] + 0.01 * Conductivity \left[\frac{mS}{cm} \right] - 2.1$.

The standard deviation was estimated to 0.4 mg/L and was based on 52 samples.

Table H-1: Comparison of values measured by ISE+Ag, Spectroquant Cell Test and recalculated values.

ISE+Ag	Spectroquant Cell Test	Recalculated value	
	5.3	5.1	4.2
	11.5	9.1	10.0
	8.3	7.3	6.8
	6.6	5.7	5.4
	6.6	5.6	5.3
	17.7	13.2	13.4
	6.6	5.3	5.2
	4.7	4	3.8
	6.2	5.1	5.0
	4.4	4.3	3.8
	4.2	4.3	3.7
	5.7	5.2	4.7
	7.4	6.2	6.0
	6.7	5.5	5.3
	7.8	6	6.3
	7.6	5.7	6.2
	6.9	5.4	5.8
	6.5	5.7	5.6
	1.8	0.2	1.4
	0.8	0.2	0.6
	0.9	0.5	0.5
	0.9	0.6	0.5

APPENDIX J: Previous data from Leikvollbekken

Water samples from inlet (Figure J-1) mid-pond (Figure J-2) and outlet (Figure J-3) in Leikvollbekken 2014/2015. Samples were taken and analyzed by Espen Enge (UiS) and Fredrik Berg-Larsen.

Table J-1: Previous data from samples taken inlet to Pond 1.

	Date	pH	Conductivity [μ S/cm]	Alk _e [μ ekv/L]	Cl ⁻ [mg/L]
Leikvoll O	22-Dec-14	6.10	239	571	20.5
Leikvoll O	23-Jan-15	6.12	310	740	32.3
Leikvoll O	10-Feb-15	6.03	284	724	29.7
Leikvoll O	4-Mar-15	5.99	297	773	22.7
Leikvoll O	11-Mar-15	6.16	324	884	25.4
Leikvoll O	18-Mar-15	6.14	320	826	27.3
Leikvoll O	25-Mar-15	6.05	286	872	25.7
Leikvoll O	8-Apr-15	6.18	330	905	31.3
Leikvoll O	13-Apr-15	6.11	327	841	31.7
Leikvoll O	20-Apr-15	6.20	346	970	30.6
Leikvoll O	28-Apr-15	6.15	365	615	30.3
Leikvoll O	12-May-15	6.18	382	602	32.5

Table J-2: Previous data from samples taken inlet to Pond 2.

	Date	pH	Conductivity [μ S/cm]	Alk _e [μ ekv/L]	Cl- [mg/L]
Leikvoll M	23-Jan-15	6.19	313	766	32.8
Leikvoll M	10-Feb-15	6.23	278	701	31.6
Leikvoll M	4-Mar-15	6.24	257	714	24.6
Leikvoll M	11-Mar-15	6.33	297	788	24.2
Leikvoll M	18-Mar-15	6.34	309	792	28.5
Leikvoll M	25-Mar-15	6.12	281	850	25.0
Leikvoll M	8-Apr-15	6.31	316	790	32.1
Leikvoll M	13-Apr-15	6.28	310	823	32.3
Leikvoll M	20-Apr-15	6.36	328	931	30.0
Leikvoll M	28-Apr-15	6.42	325	745	30.8
Leikvoll M	12-May-15	6.51	325	665	29.8

Table J-3: Previous data from samples taken outlet to Pond 2.

	Date	pH	Conductivity [μ S/cm]	Alk _e [μ ekv/L]	Cl- [mg/L]
Leikvoll N	17-Dec-14	6.31	264	640	22.9
Leikvoll N	22-Dec-14	6.28	220	539	20.4
Leikvoll N	23-Jan-15	6.37	310	799	33.6
Leikvoll N	10-Feb-15	6.38	276	704	31.0
Leikvoll N	4-Mar-15	6.40	246	674	25.3
Leikvoll N	11-Mar-15	6.51	282	748	25.9
Leikvoll N	18-Mar-15	6.69	305	788	29.0
Leikvoll N	25-Mar-15	6.35	269	850	25.1
Leikvoll N	8-Apr-15	6.60	304	814	32.8
Leikvoll N	13-Apr-15	6.66	296	828	33.2
Leikvoll N	20-Apr-15	6.71	308	893	31.7
Leikvoll N	28-Apr-15	6.72	307	933	32.0
Leikvoll N	12-May-15	6.66	310	696	29.4

APPENDIX K: pH, conductivity, alkalinity and color in reference samples.

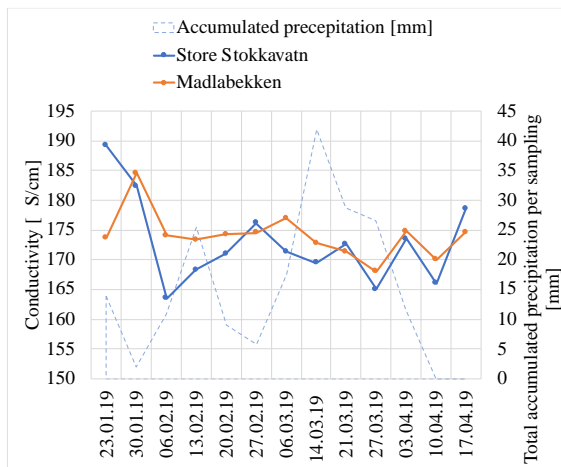


Figure K-1: Variations in conductivity in reference samples

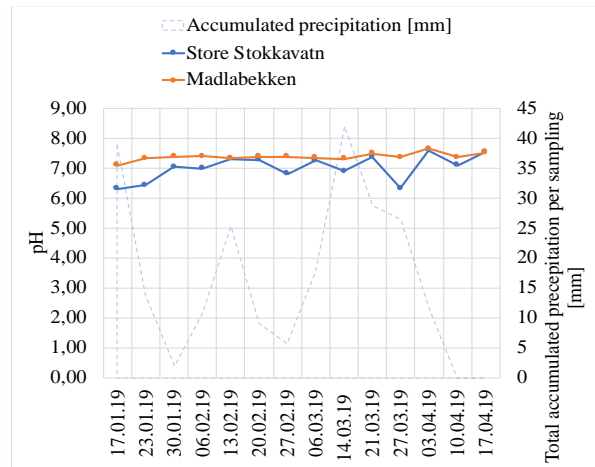


Figure K-2: Variations in pH in reference samples

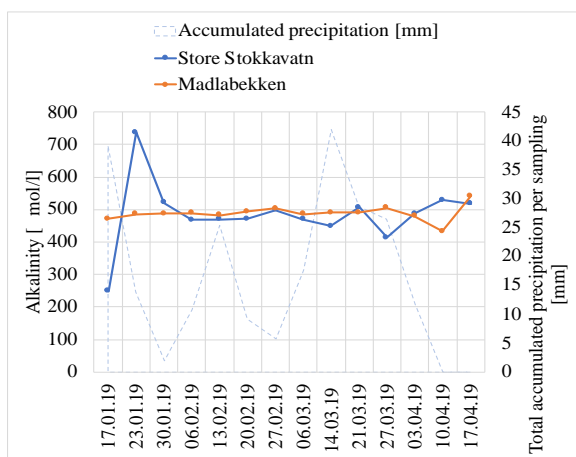


Figure K-3: Variations in alkalinity in reference samples

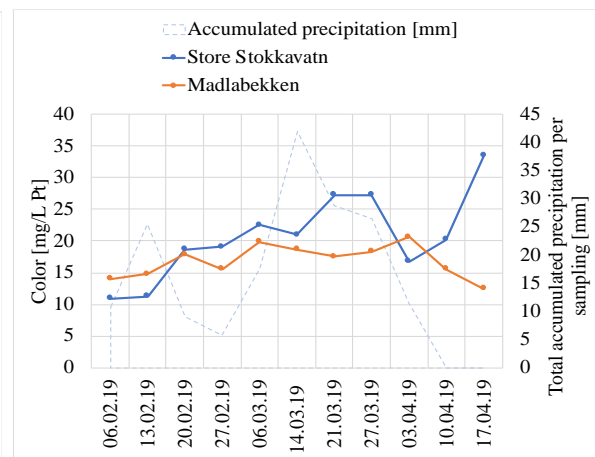


Figure K-4: Variations in color in samples